

(19)

Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 0 722 973 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
17.12.2003 Bulletin 2003/51

(51) Int Cl.7: **C08J 3/24, C08J 3/28,
A61F 2/30
// C08L23:06**

(21) Application number: **96300113.6**

(22) Date of filing: **05.01.1996**

(54) Chemically crosslinked ultrahigh molecular weight polyethylene for artificial human joints

Chemisch vernetztes ultrahochmolekulares Polyethylen für künstliche menschliche Gelenke

Polyéthylène de poids moléculaire ultra élevé chimiquement réticulé pour articulations humaines artificielles

(84) Designated Contracting States:
CH DE DK FR GB LI SE

(30) Priority: **20.01.1995 US 376953**

(43) Date of publication of application:
24.07.1996 Bulletin 1996/30

(73) Proprietors:

- THE UNIVERSITY OF SOUTHERN CALIFORNIA
Los Angeles, California 90089 (US)
- Orthopaedic Hospital
Los Angeles, California 90007-2697 (US)

(72) Inventors:

- Salovey, Ron
Rancho Palos Verdes, California 90275 (US)
- Shen, Fu-Wen
California, 91789 (US)
- McKellop, Harry A.
Los Angeles, California 90049 (US)

(74) Representative: Pearce, Anthony Richmond
**MARKS & CLERK,
Alpha Tower,
Suffolk Street Queensway
Birmingham B1 1TT (GB)**

(56) References cited:
BE-A- 1 001 574

- POLYMER, vol. 30, no. 5, May 1989, GB, pages 866-873, XP000569234 DIJKSTRA D.J. ET AL: "Cross-linking of ultra-high molecular weight polyethylene in the melt by means of electron beam Irradiation"
- POLYMER, vol. 23, no. 09, August 1982, GB, pages 1944-1952, XP000569235 DE BOER J. ET AL: "Cross-linking of ultra-high molecular weight polyethylene in the melt by means..."
- DATABASE WPI Derwent Publications Ltd., London, GB; AN 87-338571[48] XP002001745 & JP-A-62 243 634 (NIPPON OIL KK), 24 January 1987
- PATENT ABSTRACTS OF JAPAN vol. 009, no. 021 (C-263) & JP-A-59 168050 (MITSUBOSHI BELT KK), 21 September 1984,
- JOURNAL OF MACROMOLECULAR SCIENCE - PHYSICS, vol. B26, no. 1, 1987, US, pages 37-58, XP000569227 NARKIS M. ET AL: "Structure and tensile behavior of Irradiation- and peroxide-crosslinked polyethylenes"
- PATENT ABSTRACTS OF JAPAN vol. 016, no. 501 (C-0996), 16 October 1992 & JP-A-04 185651 (FUJIKURA LTD.), 2 July 1992,
- JOURNAL OF APPLIED POLYMER SCIENCE, vol. 48, 1993, US, pages 711-719, XP002001744 QU B.J.: "Photocross-linking of low-density polyethylene. II. Structure and morphology"

Remarks:

The file contains technical information submitted after the application was filed and not included in this specification

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

EP 0 722 973 B1

DescriptionTechnical Field Of The Invention

- 5 [0001] The present invention relates to polymers. It discloses a method for enhancing the wear-resistance of polymers, especially polymers that are to be irradiated, by crosslinking the polymers. The crosslinked polymers may be annealed to stabilize their size shrinkage. The polymers disclosed herein are particularly useful for making in vivo implants.

10 Background Of The Invention

[0002] Ultrahigh molecular weight polyethylene (hereinafter referred to as "UHMW polyethylene") is commonly used to make prosthetic joints such as artificial hip joints. In recent years, it has become increasingly apparent that tissue necrosis and interface osteolysis, in response to UHMW polyethylene wear debris, are primary contributors to the long-term loosening failure of prosthetic joints. For example, the process of wear of acetabular cups of UHMW polyethylene in artificial hip joints introduces many microscopic wear particles into the surrounding tissues. The reaction of the body to these particles includes inflammation and deterioration of the tissues, particularly the bone to which the prosthesis is anchored. Eventually, the prosthesis becomes painfully loose and must be revised. It is generally accepted by orthopaedic surgeons and biomaterials scientists that the reaction of tissue to wear debris is the chief cause of long-term failure of such prostheses.

15 [0003] Laboratory experiments and examination of worn polyethylene components, as used in acetabular cups of total hip prostheses, after removal from patients, have shown that polyethylene wear in vivo primarily involves three fundamental mechanisms: adhesive, abrasive, and fatigue wear (Brown, K.J., et al., Plastics in Medicine & Surgery Plastics & Rubber Institute, London, 2.1-2.5 (1975); Nusbaum, H.J. & Rose, R.M., J. Biomed. Materials Res., 13: 20 557-576 (1979); Rostoker, W., et al., J. Biomed. Materials Res., 12:317-335 (1978); Swanson, S.A.V. & Freeman, M. A.R., Chapter 3, "Friction, lubrication and wear.", The Scientific Basis of Joint Replacement, Pittman Medical Publishing Co., Ltd. (1977).}

[0004] Adhesive wear occurs when there is local bonding between asperities on the polymer and the opposing (metal or ceramic) counterface. If the ratio of the strength of the adhesive bond to the cohesive strength of the polymer is great enough, the polymer may be pulled into a fibril, finally breaking loose to form a wear particle. Small wear particles (measuring microns or less) are typically produced.

30 [0005] Abrasive wear occurs when asperities on the surface of the femoral ball, or entrapped third-body particles, penetrate into the softer polyethylene and cut or plow along the surface during sliding. Debris may be immediately formed by a cutting process, or material may be pushed to the side of the track by plastic deformation, but remain an integral part of the surface.

35 [0006] Fatigue wear is dependent on cyclic stresses applied to the polymer. As used herein, fatigue wear is an independent wear mechanism involving crack formation and propagation within the polymer. Cracks may form at the surface and coalesce, releasing wear particles as large as several millimeters and leaving behind a corresponding pit on the surface, or cracks may form a distance below the surface and travel parallel to it, eventually causing sloughing off of large parts of the surface.

40 [0007] There are gaps in the prior art regarding the contributions of the above three basic mechanisms to the wear of polyethylene cups in vivo. While numerous laboratory studies and analyses of retrieved implants have provided valuable details on wear in vivo, there is ongoing disagreement regarding which wear mechanisms predominate and what are the controlling factors for wear.

45 [0008] However, it is clear that improving the wear resistance of the UHMW polyethylene socket and, thereby, reducing the amount of wear debris generated each year, would extend the useful life of artificial joints and permit them to be used successfully in younger patients. Consequently, numerous modifications in physical properties of UHMW polyethylene have been proposed to improve its wear resistance.

50 [0009] UHMW polyethylene components are known to undergo a spontaneous, post-fabrication increase in crystallinity and changes in other physical properties. {Grood, E.S., et al., J. Biomedical Materials Res., 16:399-405 (1976); Kurth, J., et al., Trans. Third World Biomaterials Congress, 589 (1988); Rimmac, C.M., et al., J. Bone & Joint Surgery, 76-A-(7):1052-1056 (1994)}. These occur even in stored (non-implanted) cups after sterilization with gamma radiation which initiates an ongoing process of chain scission, crosslinking, and oxidation or peroxidation involving free radical formation. {Eyerer, P. & Ke, Y.C., J. Biomed. Materials Res., 18:1137-1151 (1984); Nusbaum, H. J. & Rose, R.M., J. Biomed. Materials Res., 13:557-576 (1979); Roe, R.J., et al., J. Biomed. Materials Res., 15:209-230 (1981); Shen, C. & Dumbleton, J.H., Wear, 30:349-364 (1974)}. These degradative changes may be accelerated by oxidative attack from the joint fluid and cyclic stresses applied during use. {Eyerer, P. & Ke, Y.C., J. Biomed. Materials Res., supra; Grood, E.S., et al., J. Biomed. Materials Res., supra; Rimmac, C.M., et al., ASTM Symposium on Biomaterials' Me-

chanical Properties, Pittsburgh, May 5-6 (1992)).

[0010] On the other hand, it has been reported that the best total hip prosthesis for withstanding wear is one with an alumina head and an irradiated UHMW polyethylene socket, as compared to a un-irradiated socket. The irradiated socket had been irradiated with 10^8 rad of γ -radiation, or about 40 times the usual sterilization dose. {Oonishi, H., et al., Radiat. Phys. Chem., 39(6):495-504 (1992)}. The usual average sterilization dose ranges from 2.5 to 4.0 Mrad. Other investigators did not find any significant reduction in the wear rates of UHMW polyethylene acetabular cups which had been irradiated, in the solid phase, in special atmospheres to reduce oxidation and encourage crosslinking. (Ferris, B.D., J. Exp. Path., 71:367-373 (1990); Kurth, M., et al., Trans. Third World Biomaterials Congress, 589 (1988); Roe, R.J., et al., J. Biomed. Materials Res., 15:209-230 (1981); Rose, et al., J. Bone & Joint Surcrey, 62A(4):537-549 (1980); Streicher, R.M., Plastics & Rubber Processing & Applications, 10:221-229 (1988)).

[0011] Meanwhile, DePuy.DuPont Orthopaedics has fabricated acetabular cups from conventionally extruded bar stock that has previously been subjected to heating and hydrostatic pressure that reduces fusion defects and increases the crystallinity, density, stiffness, hardness, yield strength, and resistance to creep, oxidation and fatigue. {U.S. Patent No. 5,037,928, to Li, et al., Aug. 6, 1991; Huang, D. D. & Li, S., Trans. 38th Ann. Mtg., Orthop. Res. Soc., 17:403 (1992); Li, S. & Howard, E. G., Trans. 16th Ann. Society for Biomaterials Meeting, Charleston, S.C., 190 (1990).} Silane cross-linked UHMW polyethylene (XLP) has also been used to make acetabular cups for total hip replacements in goats. In this case, the number of *in vivo* debris particles appeared to be greater for XLP than conventional UHMW polyethylene cup implants (Ferris, B. D., J. Exp. Path., 71:367-373 (1990)).

[0012] Other modifications of UHMW polyethylene have included: (a) reinforcement with carbon fibers {"Poly Two Carbon-Polyethylene Composite-A Carbon Fiber Reinforced Molded Ultra-High Molecular Weight Polyethylene", Technical Report, Zimmer (a Bristol-Myers Squibb Company), Warsaw (1977)}; and (b) post processing treatments such as solid phase compression molding {Eyerer, P., Polyethylene, Concise Encyclopedia of Medical & Dental Implant Materials, Pergamon Press, Oxford, 271-280 (1990); Li, S., et al., Trans. 16th Annual Society for Biomaterials Meeting, Charleston, S.C., 190 (1990); Seedhom, B.B., et al., Wear, 24:35-51 (1973); Zachariades, A.E., Trans. Fourth World Biomaterials Congress, 623 (1992)}. However, to date, none of these modifications has been demonstrated to provide a significant reduction in the wear rates of acetabular cups. Indeed, carbon fiber reinforced polyethylene and a heat-pressed polyethylene have shown relatively poor wear resistance when used as the tibial components of total knee prosthesis. (Bartel, D.L., et al., J. Bone & Joint Surgery, 68-A(7):1041-1051 (1986); Conelly, G.M., et al., J. Orthop. Res., 2:119-125 (1984); Wright, T.M., et al., J. Biomed. Materials Res., 15: 719-730 (1981); Bloebaum, R.D., et al., Clin. Orthop., 269:120-127 (1991); Goodman, S. & Lidgren, L., Acta Orthop. Scand., 63(3) 358-364 (1992); Landy, M. M. & Walker, P.S., J. Arthroplasty, Supplement, 3:S73-S85 (1988); Rimnac, C.M., et al., Trans. Orthopaedic Research Society, 17:330 (1992); Rimnac, C.M. et al., "Chemical and mechanical degradation of UHMW polyethylene: Preliminary report of an *in vitro* investigation," ASTM Symposium on Biomaterials' Mechanical Properties, Pittsburgh, May 5-6 (1992)).

Summary Of The Invention

[0013] One aspect of the invention presents a method for reducing the crystallinity of a polymer so that it can better withstand wear. An effective method for reducing the crystallinity of the polymer is by crosslinking. For reduction of crystallinity, the polymer may be irradiated in the melt or, preferably, chemically crosslinked in the molten state. The method is particularly useful for polymer which undergoes irradiation sterilization in the solid state. It is advantageous if the crosslinked polymer is annealed to stabilize its shrinkage.

[0014] Another aspect of the invention presents a method for making *in vivo* implants based on the above treatment of the polymer.

[0015] Another aspect of the invention presents a polymer, made from the above method, having an increased ability to withstand wear.

[0016] Another aspect of the invention presents *in vivo* implants made from the polymer described above.

[0017] The implants of the present invention are in accordance with claim 1 or 3.

[0018] The implantable bearing components of the present invention are in accordance with claim 19 or 21. Methods of making an implant or improving its wear resistance are in accordance with any one of claims 32,33,42,43,52 and 53.

Brief Description Of The Drawings

[0019] FIG. 1 presents SEM micrographs of fracture surfaces of the compression molded UHMW polyethylene (after irradiation) at magnifications of (A) x 200 and (B) x 5000.

[0020] FIG. 2 presents SEM micrographs of fracture surfaces of compression molded UHMW polyethylene crosslinked with 1 wt% peroxide (after irradiation) at magnifications of (A) x 200 and (B) x 5000.

[0021] FIG. 3 presents the geometry of the acetabular cup tested for wear on the hip joint simulator used in EXAMPLE

2 below.

[0022] FIG. 4 presents a schematic diagram of the hip joint simulator used in EXAMPLE 2 below.

[0023] FIG. 5 presents a graph comparing the amounts of wear of the modified and unmodified UHMW polyethylene cups during a run lasting a million cycles.

5

Detailed Description Of The Invention

[0024] Abbreviations used in this application are as follows:

10 DSC --

differential scanning calorimetry.

FTIR --

Fourier Transform Infrared Spectroscopy

SEM --

scanning electron microscopy

UHMW --

ultra-high molecular weight

15 UHMWPE --

ultra-high molecular weight polyethylene, also referred to as UHMW polyethylene

WAXS --

wide angle X-ray scattering

[0025] Cutting through the plethora of choices and confusion in the art, applicants discovered that a low degree of crystallinity is a major factor in increasing the ability of polyethylene to withstand wear *in vivo*, contrary to the above teaching of DePuy.DuPont Orthopaedics. Solid polymers that can crystallize generally contain both crystalline and amorphous states. These two states have different physical properties. The applicants believe that the crystalline component of polymers is more brittle and less wear-resistant than the amorphous component, the amorphous component being more ductile and more wear-resistant.

[0026] In the present invention, the degree of crystallinity of the polymer is preferably reduced by crosslinking. The crosslinking can be achieved by various methods known in the art, for example, by irradiation crosslinking of the molten polymer; photocrosslinking of the molten polymer; and crosslinking of the polymer with a free radical generating chemical. The preferred method is chemical crosslinking. As indicated, if the crosslinking is to be achieved by irradiation, the polymer should be irradiated in the melt, unlike the above mentioned prior art irradiation methods, such as in Oonishi et al. Applicants also discovered that such a crosslinked polymer is useful for *in vivo* implant because it is wear resistant. Such *in vivo* implant has not been envisioned by the prior art. Moreover, since acetabular cups are routinely sterilized by irradiation which increases the crystallinity of UHMW polyethylene {Bhateja, S.K., J. Macromol. Sci. Phys., B22:159 (1983); Bhateja, S.K., et al., J. Polym. Sci., Polym. Phys. Ed., 21:523 (1983); and Bhateja, S.K. & Andrews, E.H., J. Mater. Sci., 20:2839 (1985)}, applicants realized that the irradiation in fact makes the polymer more susceptible to wear, contrary to the teaching of the prior art such as Oonishi et al, *supra*. By crosslinking the polymer before sterilization by irradiation, applicants' method mitigates the deleterious effects of irradiation, such as chain scission. Applicants' method calls for determination of the crystallinity after irradiation to adjust the crosslinking conditions to reduce crystallinity. The polymer may also be irradiated under certain conditions e.g., in nitrogen atmosphere to reduce the immediate and subsequent amounts of oxidation. Reducing oxidation increases the amount of crosslinking. In producing acetabular cups, applicants discovered that both uncrosslinked and crosslinked cups show shrinkage in size, but crosslinked cups tend to shrink more than uncrosslinked cups. Thus, the present invention also provides for annealing the crosslinked polymer in order to shrink it to a stable size before reshaping the polymer.

[0027] Most importantly, implants which are produced by the foregoing methods of the invention are more wear resistant than conventional untreated polymer. Thus, an example of the present invention presents an UHMW polyethylene acetabular cup of a total hip prosthesis which has been chemically crosslinked by a peroxide, and then sterilized by irradiation, showing only one fifth of the wear of a control cup after a simulated year of *in vivo* use.

45

Method for Treating the Polymers

[0028] One aspect of the invention presents a method for treating a polymer to reduce its crystallinity to less than 45% to enable the resulting polymer to better withstand wear. The polymer's crystallinity is preferably reduced by crosslinking in the molten state followed by cooling to the solid state. Preferably, the crosslinking reduces the crystallinity of the polymer by about 10% to 50%; more preferably, by about 10% to 40%; and most preferably, by about 10% to 30% compared to an uncrosslinked polymer. For example, the preferable degree of crystallinity of crosslinked UHMW polyethylene is between about 24% to 44%; more preferably, between 29% to 44%; and most preferably, between about 34% to 44%. After sterilization by irradiation, the crosslinked polymer has a reduced crystallinity compared to the uncrosslinked polymer. Preferably, the irradiated crosslinked polymer possesses about 10% to 50%; more preferably, about 10% to 40%; and most preferably, about 10% to 30% less degree of crystallinity compared to the uncrosslinked but irradiated polymer. For example, the preferable degree of crystallinity of irradiated, crosslinked UHMW polyethylene is between about 28% to 51%; more preferably, between about 33% to 51%; and most preferably, between

about 39% to 51%. For example, EXAMPLE 1, Table 1 below shows the degree of crystallinity for UHMW polyethylene containing different weight percentage of peroxide. In the following EXAMPLE 2, UHMW polyethylene which was crosslinked by 1% weight (wt) peroxide exhibited about 39.8% crystallinity, i.e. about a 19% reduction in crystallinity compared to uncrosslinked UHMW polyethylene which possessed about 49.2% crystallinity. After gamma irradiation

5 to an average dose of about 3.4 Mrad, the crosslinked UHMW polyethylene exhibits about 42% crystallinity, i.e., a reduction of about 25% in crystallinity compared to the originally uncrosslinked but radiation sterilized UHMW polyethylene which possessed about 55.8% crystallinity. Thus, it is contemplated that after the usual sterilization dosage in the solid state, which generally averages between 2.5 to 4.0 Mrad, the treated polymer preferably possesses less than about 45% crystallinity, and more preferably about 42% crystallinity or less. Also, the treated polymer preferably possesses less than about 43%, more preferably less than about 40%, crystallinity before irradiation in the solid state.

10 [0029] If the polymer is to be molded, e.g. as an acetabular cup, the polymer may be placed in the mold and crosslinked therein. Further crosslinking examples are: (1) irradiation of the polymer when it is in a molten state, e.g. UHMW polyethylene has been crosslinked in the melt by electron beam irradiation; and molten linear polyethylene has been irradiated with fast electrons (Dijkstra, D.J. et al., *Polymer*, **30**:866-709 (1989); Gielenz G. & Jungnickle, B.J., *Colloid & Polymer Sci.*, **260**:742-753 (1982)); the polymer may also be gamma-irradiated in the melt; and (2) photo-crosslinking of the polymer in the melt, e.g. polyethylene and low-density polyethylene have been photocrosslinked {Chen, Y.L. & Ranby, B., *J. Polymer Sci.: Part A: Polymer Chemistry*, **27**:4051-4075, 4077-4086 (1989)}; Qu, B.J. & Ranby, B., *J. Applied Polymer Sci.*, **48**:711-719 (1993)).

20 Choices of Polymers

[0030] The polymers are generally polyhydrocarbons. Ductile polymers that wear well are preferred. Examples of such polymers include: polyethylene, polypropylene, polyester and polycarbonates. For example, UHMW polymers may be used, such as UHMW polyethylene and UHMW polypropylene. An UHMW polymer is a polymer having a molecular weight (MW) of at least about a million.

25 [0031] For *in vivo* implants, the preferred polymers are those that are wear resistant and have exceptional chemical resistance. UHMW polyethylene is the most preferred polymer as it is known for these properties and is currently widely used to make acetabular cups for total hip prostheses. Examples of UHMW polyethylene are: Hostalen GUR 415 medical grade UHMW polyethylene flake (Hoechst-Celanese Corporation, League City, Texas), with a weight average 30 molecular weight of 6×10^6 MW; Hostalen GUR 412 with a weight average molecular weight of between 2.5×10^6 to 3×10^6 MW; Hostalen GUR 413 of 3×10^6 to 4×10^6 MW; RCH 1000 (Hoechst-Celanese Corp.); and HiFax 1900 of 4×10^6 MW (HiMont, Elkton, Maryland). GUR 412, 413 and 415 are in the form of powder. RCH 1000 is usually available as compression molded bars. Historically, companies which make implants have used GUR 412 and GUR 415 for making acetabular cups. Recently, Hoechst-Celanese Corp. changed the designation of GUR 415 to 4150 resin and indicated that 4150 HP was for use in medical implants.

Methods for Characterizing the Polymers (Especially the Determination of Their Crystallinity)

[0032] The degree of crystallinity of the crosslinked polymer may be determined after it has been crosslinked or 40 molded. In case the treated polymer is further irradiated, e.g., to sterilize the polymer before its implant into humans, the degree of crystallinity may be determined after irradiation, since irradiation effects further crystallization of the polymer.

[0033] The degree of crystallinity can be determined using methods known in the art, e.g. by differential scanning 45 calorimetry (DSC), which is generally used to assess the crystallinity and melting behavior of a polymer. Wang, X. & Salovey, R., *J. App. Polymer Sci.*, **34**: 593-599 (1987).

[0034] X-ray scattering from the resulting polymer can also be used to further confirm the degree of crystallinity of the polymer, e.g. as described in Spruiell, J.E., & Clark, E.S., in "Methods of Experimental Physics", L. Marton & C. Marton, Eds., Vol. 16, Part B, Academic Press, New York (1980). Swelling is generally used to characterize crosslink distributions in polymers, the procedure is described in Ding, Z. Y., et al., *J. Polymer Sci., Polymer Chem.*, **29**: 1035-38 50 (1990). Another method for determining the degree of crystallinity of the resulting polymer may include FTIR {Painter, P.C. et al., "The Theory Of Vibrational Spectroscopy And Its Application To Polymeric Materials", John Wiley and Sons, New York, U.S.A. (1982)} and electron diffraction. FTIR assesses the depth profiles of oxidation as well as other chemical changes such as unsaturation (Nagy, E.V., & Li, S., "A Fourier transform infrared technique for the evaluation of polyethylene orthopaedic bearing materials", *Trans. Soc. for Biomaterials*, **13**:109 (1990); Shinde, A. & Salovey, R., *J. Polymer Sci., Polym. Phys. Ed.*, **23**:1681-1689 (1985)). A further method for determining the degree of crystallinity of 55 the resulting polymer may include density measurement according to ASTM D1505-68.

Methods for Chemically Crosslinking the Polymers

[0035] The polymer is preferably chemically crosslinked to decrease its crystallinity. Preferably, the crosslinking chemical, i.e. a free radical generating chemical, has a long half-life at the molding temperature of the chosen polymer.

5 The molding temperature is the temperature at which the polymer is molded. The molding temperature is generally at or above the melting temperature of polymer. If the crosslinking chemical has a long half-life at the molding temperature, it will decompose slowly, and the resulting free radicals can diffuse in the polymer to form a homogeneous crosslinked network at the molding temperature. Thus, the molding temperature is also preferably high enough to allow the flow of the polymer to occur to distribute or diffuse the crosslinking chemical and the resulting free radicals to form the homogeneous network. For UHMW polyethylene, the molding temperature is between 150° to 220°C and the molding time is between 1 to 3 hours; the preferable molding temperature and time being 170°C and 2 hours, respectively.

10 [0036] Thus, the crosslinking chemical may be any chemical that decomposes at the molding temperature to form highly reactive intermediates, free radicals, which would react with the polymers to form the crosslinked network. Examples of free radical generating chemicals are peroxides, peresters, azo compounds, disulfides, dimethacrylates, tetrazenes, and divinyl benzene. Examples of azo compounds are: azobisisobutyronitrile, azobisisobutyronitrile, and dimethylazodi isobutyrate. Examples of peresters are t-butyl peracetate and t-butyl perbenzoate.

15 [0037] Preferably the polymer is crosslinked by treating it with an organic peroxide. The preferable peroxides are 2,5-dimethyl-2,5-bis(tert-butylperoxy)-3-hexyne (Lupersol 130, Atochem Inc., Philadelphia, Pennsylvania); 2,5-dimethyl-2,5-di-(t-butylperoxy)-hexane; t-butyl α-cumyl peroxide; di-butyl peroxide; t-butyl hydroperoxide; benzoyl peroxide; 20 dichlorobenzoyl peroxide; dicumyl peroxide; di-tertiary butyl peroxide; 2,5 dimethyl-2,5 di(peroxy benzoate) hexyne-3; 1,3-bis(t-butyl peroxy isopropyl) benzene; lauroyl peroxide; di-t-amyl peroxide; 1,1-di-(t-butylperoxy) cyclohexane; 2,2-di-(t-butylperoxy)butane; and 2,2-di-(t-amylperoxy) propane. The more preferred peroxide is 2,5-dimethyl-2,5-bis (tert-butylperoxy)-3-hexyne. The preferred peroxides have a half-life of between 2 minutes to 1 hour; and more preferably, the half-life is between 5 minutes to 50 minutes at the molding temperature.

25 [0038] Generally, between 0.2 to 5.0 wt% of peroxide is used; more preferably, the range is between 0.5 to 3.0 wt% of peroxide; and most preferably, the range is between 0.6 to 2 wt%.

[0039] The peroxide can be dissolved in an inert solvent before being added to the polymer powder. The inert solvent preferably evaporates before the polymer is molded. Examples of such inert solvents are alcohol and acetone.

30 [0040] For convenience, the reaction between the polymer and the crosslinking chemical, such as peroxide, can generally be carried out at molding pressures. Generally, the reactants are incubated at molding temperature, between 1 to 3 hours, and more preferably, for about 2 hours.

[0041] The reaction mixture is preferably slowly heated to achieve the molding temperature. After the incubation period, the crosslinked polymer is preferably slowly cooled down to room temperature. For example, the polymer may be left at room temperature and allowed to cool on its own. Slow cooling allows the formation of a stable crystalline structure.

35 [0042] The reaction parameters for crosslinking polymers with peroxide, and the choices of peroxides, can be determined by one skilled in the art. For example, a wide variety of peroxides are available for reaction with polyolefins, and investigations of their relative efficiencies have been reported {Lem, K.W. & Han, C.D., *J. Appl. Polym. Sci.*, **27**: 1367 (1982); Kampouris, E.M. & Andreopoulos, A.G., *J. Appl. Polym. Sci.*, **34**:1209 (1987) and Bremner, T. & Rudin, *A. J. Appl. Polym. Sci.*, **49**:785 (1993)}. Differences in decomposition rates are perhaps the main factor in selecting a particular peroxide for an intended application {Bremner, T. & Rudin, *A. J. Appl. Polym. Sci.*, **49**:785 (1993)}. Bremner and Rudin, *Id.*, compared three dialkyl peroxides on the basis of their ability to increase the gel content, crosslinking efficiency, and storage modulus of virgin polyethylene through a crosslinking mechanism and found that they decreased in the order of α,α-bis(tertiary butylperoxy)-p-diisopropyl benzene > dicumyl peroxide > 2,5-dimethyl-2,5-di-(tertiary butylperoxy)-hexyne-3 at the same active peroxide radical concentrations and temperature.

40 [0043] More specifically, peroxide crosslinking of UHMW polyethylene has also been reported {de Boer, J. & Pennings, A.J., *Makromol. Chem. Rapid Commun.*, **2**:749 (1981); de Boer, J. & Pennings, A.J., *Polymer*, **23**:1944 (1982); de Boer, J., *et al.*, *Polymer*, **25**:513 (1984) and Narkis, M., *et al.*, *J. Macromol. Sci. Phys.*, **B** **26**:37, 58 (1987)}. de Boer *et al.* crosslinked UHMW polyethylene in the melt at 180°C by means of 2,5-dimethyl-2,5-di-(tert-butylperoxy)-hexyne-3 and found that crosslinks and entanglements, whether trapped or not, contributed to the same degree to the decrease in crystallinity of UHMW polyethylene upon crosslinking (de Boer, J. & Pennings, A.J., *Polymer*, **23**:1944 (1982)). It was concluded that an almost completely crosslinked (or gelled) material with high crystallinity and good mechanical properties could be obtained by using as little as 0.2-0.3 wt% of peroxide.

45 [0044] Some of the above references investigated the effect of peroxide crosslinking on UHMW polyethylene, such as in lowering crystallinity; and the effects of reaction parameters, such as peroxide concentrations {de Boer, J. & Pennings, A.J., *Polymer*, **23**:1944 (1982); Narkis, M., *et al.*, *J. Macromol. Sci. Phys.*, **B** **26**:37-58 (1987)}. However, these references do not address the effect of peroxide crosslinking or the lowering of crystallinity in relation to the wear property of the resulting polymer. For example, de Boer and Pennings, in *Polymer*, **23**:1944 (1982), were concerned

with the effect of crosslinking on the crystallization behavior and the tensile properties of UHMW polyethylene. The authors found that tensile properties, such as tensile strength at break point and Young's modulus, of the UHMW polyethylene, showed a tendency to decrease with increasing peroxide content.

[0045] Similarly, Narkis, M., et al., *J. Macromol. Sci. Phys.*, B 26:37-58 (1987), separately determined the effects of 5 irradiation and peroxide on the crosslinking and degree of crystallinity of UHMW polyethylene (Hostalen GUR 412), high molecular weight polyethylene, and normal molecular weight polyethylene. However, M. Narkis et al., did not study the inter-relationship of peroxide crosslinking and irradiation, nor their effects on wear resistance.

Use of Crosslinked Polymers for In Vivo Implants

[0046] Another aspect of the invention presents a process for making in vivo implants using the above chemically 10 crosslinked polymer. Since in vivo implants are often irradiated to sterilize them before implant, the present invention provides the further step of selecting for implant use, a polymer with about 45% crystallinity or less after irradiation sterilization. For γ -irradiation sterilization, the minimum dosage is generally 2.5 Mrad. The sterilization dosage generally 15 falls between 2.5 and 4.0 Mrad. The preferable degree of crystallinity is between 25% to 45% crystallinity. In EXAMPLE 2 below, the polymer has about 39.8% crystallinity after crosslinking; and about 42% crystallinity after further irradiation with γ -radiation to an average dose of about 3.4 Mrad. Thus, the chemically crosslinked UHMW polymer preferably possesses less than about 43% crystallinity before irradiation in the solid state, and less than about 45% crystallinity 20 after irradiation with γ -radiation to an average dose of about 3.4 Mrad.

Annealing of Crosslinked Polymers

[0047] Applicants observed that both crosslinked and uncrosslinked polymers tended to shrink, but the crosslinked 25 polymer tended to shrink more than the uncrosslinked polymer (see EXAMPLE 3 below). Thus, the present invention further provides for annealing a polymer to pre-shrink it to a size which will not shrink further (i.e. stabilize the polymer's shrinkage or size). Thus, one aspect of the invention provides for a method of: 1) crosslinking a polymer, 2) selecting a crosslinked polymer of reduced crystallinity, 3) annealing the polymer to stabilize its size. Thus, the polymer can be molded at a size larger than desired, and the molded polymer is then annealed to stabilize its size. After size stabilization, the molded polymer is then resized, such as by machining, into a product with the desired dimension.

[0048] The annealing temperature is preferably chosen to avoid thermal oxidation of the crosslinked polymer which 30 will increase its crystallinity. Thus, the annealing temperature is preferably below the melting point of the molded polymer before irradiation. For example, the melting temperatures of molded UHMW polyethylene and molded 1 wt% peroxide UHMW polyethylene are 132.6°C and 122.3°C, before irradiation, respectively. The preferable annealing temperature for both these molded UHMW polyethylenes is between 60°C to 120°C, before irradiation, and more preferably 100°C. 35 These temperatures were determined by observation, based on experiments, of their minimal effect on thermal oxidation of the molded polymers. The annealing time is generally between 1 to 6 hours, and more preferably between 2 to 4 hours. In the case of UHMW polyethylene, the annealing time is preferably between 2 to 4 hours, and more preferably about 2 hours.

[0049] To further avoid thermal oxidation of the crosslinked polymer, the annealing is most preferably conducted in 40 a vacuum oven.

[0050] To ensure that the crosslinked and annealed polymer has the desired degree of crystallinity, its degree of 45 crystallinity is preferably determined after the annealing process, using the method(s) described previously.

Wear-Resistant Polymers

[0051] Another aspect of the invention presents a polymer with 45% of crystallinity or less, in particular, after irradiation 50 in the solid state and/or annealing. In EXAMPLE 2 below, the polymer has about 39.8% crystallinity after crosslinking; and about 42% crystallinity, after further irradiation with γ -radiation to an average dose of about 3.4 Mrad; or about 40.8% crystallinity, after crosslinking and annealing, but before irradiation in the solid state.

[0052] The polymers of the present invention can be used in any situation where a polymer, especially UHMW polyethylene, is called for, but especially in situations where high wear resistance is desired and irradiation of the solid 55 polymer is called for. More particularly, these polymers are useful for making in vivo implants.

In Vivo Implants Made of Crosslinked Polymers

[0053] An important aspect of this invention presents in vivo implants that are made with the above polymers or according to the method presented herein. These implants are more wear resistant than their untreated counterpart, especially after irradiation. In particular, these in vivo implants are chemically crosslinked UHMW polymers, which have 55

been molded, annealed, and resized into the shape of the implants. Further, the chemically crosslinked UHMW polymer preferably possesses less than about 43% crystallinity before irradiation in the solid state, and less than about 45% crystallinity, after γ -irradiation to an average dose of 3.4 Mrad, in the solid state. The modified polymer can be used to make in vivo implants for various parts of the body, such as components of a joint in the body. For example, in the hip joints, the modified polymer can be used to make the acetabular cup, or the insert or liner of the cup, or trunnion bearings (e.g. between the modular head and the stem). In the knee joint, the modified polymer can be used to make the tibial plateau (femoro-tibial articulation), the patellar button (patello-femoral articulation), and trunnion or other bearing components, depending on the design of the artificial knee joint. In the ankle joint, the modified polymer can be used to make the talar surface (tibio-talar articulation) and other bearing components. In the elbow joint, the modified polymer can be used to make the radio-humeral joint, ulno-humeral joint, and other bearing components. In the shoulder joint, the modified polymer can be used to make the glenoro-humeral articulation, and other bearing components. In the spine, the modified polymer can be used to make intervertebral disk replacement and facet joint replacement. The modified polymer can also be made into temporo-mandibular joint (jaw) and finger joints. The above are by way of example, and are not meant to be limiting.

Having described what the applicants believe their invention to be, the following examples are presented to illustrate the invention, and are not to be construed as limiting the scope of the invention.

EXAMPLES

EXAMPLE 1

Experimental Details

[0055] Commercial-grade UHMW polyethylene GUR 415 (from Hoechst-Celanese Corporation, League City, Texas), with a weight average molecular weight of 6×10^6 , was used as received. The peroxide used was 2,5-dimethyl-2,5-bis (tert-butylperoxy)-3-hexyne (Lupersol 130, Atochem Inc., Philadelphia, Pennsylvania). The reason for choosing Lupersol 130 was its long half-life at elevated temperature. The peroxide will decompose slowly, and the resultant free radicals can diffuse in the specimen to form a homogeneous network at elevated temperatures.

[0056] Mixing of the UHMW polyethylene and the peroxide was accomplished by dispersing polyethylene powder in an acetone solution of the peroxide and subsequently evaporating the solvent (de Boer, J., et al., *J. Polym. Sci., Polym. Phys. Ed.*, **14**:187 (1976); de Boer, J. & Pennings, A.J., *Makromol. Chem, Rapid Commun.*, **2**:749 (1981) and de Boer, J. & Pennings, A.J., *Polymer*, **23**:1944 (1982)). The mixed powder (22g) was poured into the mold cavity and then compression molded in a mold between two stainless-steel plates at 120°C and ram pressure 11×10^3 kPa for 10 minutes in order to evacuate the trapped air in the powder. After pressing, the pressure was reduced to 7.5×10^3 kPa and the specimen was heated to 170°C by circulated heating oil. These conditions were held for 2 hours. The half-life time of peroxide at 170°C in dodecane is about 9 minutes. After 2 hours, pressure was increased to 15×10^3 kPa to avoid cavities in the specimen and sink marks on the surface and the specimen was slowly cooled in the mold to room temperature. The mold was in the shape of an acetabular cup for a total hip prosthesis.

[0057] The specimens were irradiated with γ -rays at room temperature in air atmosphere by SteriGenics International (Tustin, California). Cobalt-60 was used as a source of gamma irradiation. The radiation doses were delivered at a dose rate of 5 kGy/hr. Specimens received doses to an average of about 34 kGy (i.e., an average of about 3.4 Mrad).

[0058] The physical properties of specimens before and after irradiation were characterized by DSC, equilibrium swelling, FTIR, and WAXS measurements. Surface morphology was examined by SEM.

Results and Discussion

[0059] Before irradiation, the degree of crystallinity, peak melting temperature, and recrystallization temperature for the peroxide-free specimen are 49.2%, 132.6 and 115.5°C, respectively. For a 1 wt% peroxide specimen, the degree of crystallinity, peak melting temperature, and recrystallization temperature are reduced to 39.8%, 122.3 and 110.1°C, respectively. Peroxide crosslinking reactions are accompanied by the decomposition of peroxide and abstraction of hydrogen atoms, and the resulting combination of alkyl radicals to produce carbon-carbon crosslinks. Generally, this reaction was performed above the melting temperature of the polymer. Thus the crosslinking step preceded the crystallization step. It was suggested that crystallization from a crosslinked melt produced an imperfect crystal, and crosslinks suppressed crystal growth, resulting in the depression of melting temperature and a decreased crystallinity (decreased crystallite size) (de Boer, J. et al., *J. Polym. Sci., Polym. Phys. Ed.*, **14**:187 (1976); de Boer, J. & Pennings, A.J., *Makromol. Chem, Rapid Commun.*, **2**:749 (1981); de Boer, J. & Pennings, A.J., *Polymer*, **23**:1944 (1982) and Narkis, M., et al., *J. Macromol. Sci. Phys.*, **B26**:37 (1987)). Wide-angle x-ray scattering shows that the degree of crystallinity, crystal perfection and size decrease after peroxide crosslinking. For swelling measurement, the peroxide-free

specimen dissolves completely in boiling p-xylene. The gel content, degree of swelling, and average molecular weight between crosslinks for the 1 wt% peroxide specimen are 99.6%, 2.53, and 1322 (g/mol), respectively. Because of the extremely long polymer chains in UHMW polyethylene, only a few crosslinks were needed for gelation. In addition, an almost 100% gel can be obtained by peroxide crosslinking because no chain scission occurs by peroxide crosslinking.

[0060] After irradiation, the degree of crystallinity and peak melting temperature for the peroxide-free specimen were increased to 55.8% and 135°C, respectively. It was suggested that irradiation-induced scission of taut tie molecules permits recrystallization of broken chains from the noncrystalline regions, and results in an increase in the degree of crystallinity and an increased perfection of existing folded chain crystallites (Narkis, M., et al., *J. Macromol. Sci. Phys.*, **B26**:37 (1987); Bhateja, S.K., *J. Macromol. Sci. Phys.*, **B22**:159 (1983); Bhateja, S.K., et al., *J. Polym. Sci., Polym. Phys. Ed.*, **21**:523 (1983); Kamel, I. & Finegold, L., *J. Polym. Sci., Polym. Phys. Ed.*, **23**:2407 (1985); Shinde, A. & Salovey, R., *J. Polym. Sci., Polym. Phys. Ed.*, **23**:1681 (1985); Bhateja, S.K. & Andrews, E.H., *J. Mater. Sci.*, **20**:2839 (1985); Minkova, L., *Colloid Polym. Sci.*, **266**:6 (1988); Minkova, L. & Mihailov, M., *Colloid Polym. Sci.*, **268**:1018 (1990) and Zhao, Y., et al., *J. Appl. Polym. Sci.*, **50**:1797 (1993)). The gel content after irradiation for the peroxide-free specimen was 70.8%.

[0061] For the 1 wt% peroxide specimen, the degree of crystallinity and peak melting temperature after irradiation were increased to 42% (about 2% increase) and 125.1°C, respectively. The gel content decreased to 97.5% after irradiation, whereas, the degree of swelling and molecular weight between crosslinks increased to 3.35 and 2782 (g/mol), respectively. Apparently, irradiation-induced scission of taut tie molecules resulted in a decreased gel content and an increased degree of swelling. However, after peroxide crosslinking, the effect of irradiation on network properties was mitigated. As a result of peroxide crosslinking, radiation-induced chain scission becomes less important in determining gel content. We suggest that peroxide crosslinking reduces the effect of irradiation on the crosslinked network because crosslinks introduced by peroxide crosslinking stabilize chain fragments resulting from the scission of taut tie molecules and suppress recrystallization of broken chains. Wide-angle x-ray scattering showed that crystal perfection increased after irradiation. It is suggested that crystal perfection was improved by irradiation-induced scission of taut tie molecules in the amorphous regions.

[0062] FTIR measurements showed that, after irradiation, the carbonyl concentration significantly increased. This is because the free radicals produced by irradiation reacted with oxygen dissolved and/or diffused in the polymer. In addition, the carbonyl concentration in irradiated peroxide-crosslinked samples was higher, compared to the peroxide-free sample (after irradiation). Peroxide crosslinking produces tertiary carbons, therefore, the concentration of tertiary carbons increases with increasing peroxide concentration. Applicants believe that tertiary carbons are more susceptible to oxidation during irradiation. Therefore, carbonyl concentration in the irradiated peroxide-crosslinked samples increased with increasing peroxide concentration.

[0063] After irradiation, scanning electron micrographs were taken of the fracture surfaces of the peroxide-free and 1 wt% peroxide specimens, compression molded at 170°C for 2 hours and subsequently slowly cooled to room temperature. The micrographs are shown in Figs. 1 and 2, respectively. As shown in Fig. 1, a brittle (rough) fracture boundary of size comparable to that of the original UHMW polyethylene powder particles is observed. Close examination (x 5000 magnification) shows an oriented nodular structure, composed of many smooth, submicron spheres. These smooth, minute spheres are believed to correspond to those present in the raw UHMW polyethylene powder and to form an aggregate. In Fig. 2, peroxide crosslinked samples show a ductile (smooth) fracture surface, compared to the rough fracture surface of peroxide-free specimen. The difference in appearance of fracture surfaces for peroxide-free and 1 wt% peroxide specimens is due to the crystallinity difference. After irradiation, the degree of crystallinity for the peroxide-free and 1 wt% peroxide specimens were 55.8 and 42%, respectively. It is believed that the peroxide-free specimen (55.8% crystallinity) suffered higher forces and less deformation during the fracturing process, leading to a sharp break in the polymer.

[0064] The crosslinking experiment was also conducted with different concentrations of Lupersol 130, using a smaller amount, 5 g, of GUR 415 and a smaller mold which was in the form of a disk. It was observed that the degree of crystallinity of the crosslinked polymer decreased with increased concentrations of Lupersol 130. The result is shown in Table 1 below:

TABLE 1

wt% Peroxide	Crystallinity (%) Before Irradiation	Crystallinity (%) After Irradiation
0	49.2	55.8
0.2	44.0	50.0
0.4	41.6	46.8
0.6	41.3	46.2

TABLE 1 (continued)

wt% Peroxide	Crystallinity (%) Before Irradiation	Crystallinity (%) After Irradiation
0.8	40.0	45.0
1.0	39.8	42.0
1.5	36.8	36.8
2.0	36.5	36.7

10 Conclusions

15 [0065] Peroxide crosslinking leads to a decrease in the degree of crystallinity, peak melting temperatures, and re-crystallization temperatures for 1 wt% peroxide specimen. Irradiation produces crosslinking in amorphous regions plus extensive scission of taut tie molecules and leads to increased crystallinity and crystal perfection, reduces gel content, and increases the degree of swelling of a crosslinked network.

20 [0066] Peroxide crosslinking reduces the effect of irradiation on the crosslinked network. This is because crosslinks introduced by peroxide crosslinking can stabilize the chain fragments resulting from the scission of taut tie molecules and suppress recrystallization of broken chains.

25 [0067] FTIR measurements showed that, after irradiation, the carbonyl concentration significantly increased. This is because the free radicals produced by irradiation react with oxygen dissolved and/or diffused in the polymer. In addition, carbonyl concentration in the irradiated peroxide-crosslinked samples is higher, compared to the peroxide-free sample (after irradiation). This is because peroxide crosslinking introduces tertiary carbons which are more susceptible to oxidation during irradiation, so that the carbonyl concentration in the irradiated peroxide-crosslinked samples increases.

30 [0068] Wide-angle x-ray scattering shows that crystal perfection increases after irradiation. It is suggested that crystal perfection is improved by irradiation-induced scission of taut tie molecules in the amorphous regions.

35 [0069] The peroxide-free specimen shows brittle fracture because of higher crystallinity (55.8%), whereas, the 1 wt% peroxide specimen shows ductile fracture due to lower crystallinity (42%).

30 EXAMPLE 2

Materials and Methods

40 [0070] In this example, the wear resistance of the polyethylenes treated (modified) and untreated (unmodified) with peroxide in EXAMPLE 1 were tested. The control (unmodified) and modified polyethylenes were compression molded directly into the form of acetabular cups. These were then exposed to an average of approximately 3.4 Mrad of gamma radiation (SteriGenics International, Tustin, California), to simulate the condition of cups that would be used in patients. Due to different amounts of post-molding shrinkage, the internal surface of each cup was machined to provide nearly identical internal diameters and ball-to-cup clearances among the control and modified cups (Fig. 3). As shown in Fig. 3B, the cup's outer radius 1 is 24.5 mm, its inner radius 2 is 16.1 mm, its height 3 is 29.8 mm, and its diameter 4 is 49.0 mm

45 [0071] The cups were pre-soaked in distilled water for three weeks prior to the wear test to minimize fluid absorption during the wear test. The wear cups were mounted on the hip joint simulator, including four cups of control polyethylene and three cups of modified polyethylene. Each cup was held in a urethane mold and mounted in a stainless steel test chamber, with a plexiglass wall to contain the bovine serum lubricant. The lubricant had 0.2% sodium azide added to retard bacterial degradation, and 20 milli-Molar ethylene-diaminetetraacetic acid (EDTA) to prevent precipitation of calcium phosphate on the surfaces of the ball (McKellop, H. & Lu, B., "Friction and Wear of Polyethylene-Metal and Polyethylene-Ceramic Hip Prostheses on a Joint Simulator, Fourth World Biomaterials Congress, Berlin, Apr. 1992, 118). A polyethylene skirt covered each chamber to minimize air-borne contamination. The cups were oscillated against highly polished femoral balls of cast cobalt-chromium alloy, as used on artificial hips. The simulator applied a Paul-type cyclic load at one cycle per second {Paul, J.P., *Proc. Instn. Mech. Engrs.*, 181, Part 3J, 8-15, (1967)} with a 2000N peak, simulating the load on the human hip during normal walking, and the cups were oscillated through a bi-axial 46 degree arc at 68 cycles per minute. At intervals of 250,000 cycles, the cups were removed from the wear machine, rinsed, inspected and replaced with fresh lubricant. At 500,000 cycles and one million cycles, all of the cups were 50 removed from the wear simulator, cleaned, dried and weighed to determine the weight loss due to wear. One million cycles is the equivalent of about one year's use of a prosthetic hip in a patient. Fig. 4 presents a schematic diagram of the hip joint simulator. The arrow indicates the direction of the computer controlled simulated physiological load exerted on the simulated hip joint. The simulator contains: a torque transducer 5, the acetabular cup 6, a dual axis 55

offset drive block 7, a test chamber 8, serum 9, and a femoral head 10.

[0072] Three soak-correction acetabular cups of each material (control and modified) were prepared in an identical manner, but were not wear tested. These cups were mounted in a separate test frame and a cyclic load, identical to that used in the wear test, was applied. These soak-correction cups were cleaned and weighed together with the wear test cups, and the average weight gain of the correction cups was added to the apparent weight loss of the wear test cups (i.e. to correct for fluid absorption by the wear test cups that would obscure the weight loss due to wear).

Results and Discussion

[0073] Because of the apparent "negative" wear at 0.5 million cycles (discussed below), the wear rates were calculated and compared for all of the cups only for the interval from 0.5 to 1.0 million cycles. The four control polyethylene cups showed comparable amounts of wear (Fig. 5), with an average corrected wear rate of 19.19 (S.D.=2.38) milligrams per million cycles (Table 2). This was within the range that applicants have measured for cups of conventional UHMW polyethylene in a variety of studies that applicants have run.

[0074] The wear was much lower for the modified cups (Fig. 5). As shown in Table 2, the mean wear rate for the modified cups was 4.12 (S.D.=1.26) milligrams per million cycles, i.e. about one-fifth of the wear of the control cups. This difference was statistically significant at the level of p=0.0002.

TABLE 2

WEAR RATES FOR CONTROL AND MODIFIED POLYETHYLENES (INTERVAL FROM 0.5 TO 1.0 MILLION CYCLES)			
MATERIAL	CUP NUMBER	WEAR RATE (mg/million cycles)	MEAN WEAR RATE (STANDARD DEVIATION)
CONTROL POLYETHYLENE	C2	21.67	19.19 (2.38)
	C3	16.78	
	C4	17.57	
	C9	20.76	
MODIFIED POLYETHYLENE	M4	4.08	4.12 (1.26)
	M5	2.88	
	M7	5.39	

[0075] For the data point at 0.5 million cycles, the corrected weights were lower than the weights before the wear test. This was most likely the result of the wear being very small, and the fluid absorption by the test cups being slightly greater than the average gain of the soak correction cups, such that the correction factor did not entirely offset the fluid gain by the wear cups (giving an apparent "negative" wear). A small difference in water absorption rates between the wear cups and the correction cups could arise due to differences in equilibrium temperatures (the wear cups were typically at 35°C to 45°C, whereas the soak correction cups were at room temperature, about 20°C), due to mechanical agitation of the serum during oscillation of the wear test chambers, or other causes.

EXAMPLE 3

[0076] During the wear test in the simulator described in EXAMPLE 2, it was discovered that the acetabular cups shrank at simulated human body temperature. In order to stabilize the shrinkage, in this experiment (unrelated to EXAMPLE 2), the cups were annealed at 100°C in a vacuum oven for 2 hours. After annealing, the total shrinkage in diameter for uncrosslinked and crosslinked cups was approximately 1% and 2%, respectively. The degrees of crystallinity of the annealed cups were determined by DSC. The degree of crystallinity of the uncrosslinked polymer was unchanged, whereas that of the crosslinked polymer was increased by approximately 1%. To test for further shrinkage, the cups were again put in the vacuum oven at 80°C for two hours, and no further shrinkage was observed.

[0077] The present invention has been described with reference to specific embodiments. However, this application is intended to cover those changes and substitutions which may be made by those skilled in the art without departing from the scope of the appended claims.

Claims

1. An implant for use within a body, said implant being made of irradiated crosslinked ultrahigh molecular weight polyethylene having a polymeric structure of between 28% and 51% crystallinity as measured by DSC, so as to increase the wear resistance of said implant within the body.
2. The implant of claim 1, wherein the implant is further sterilised, the crystallinity being as measured after the sterilisation.
3. An implant for use within a body, said implant being made of a crosslinked ultrahigh molecular weight polyethylene having a polymeric structure of less than 45% crystallinity as measured by DSC, so as to increase the wear resistance of said implant within the body.
4. The implant of claim 3, wherein said ultrahigh molecular weight polyethylene has between 24% to 44% crystallinity as measured by DSC.
5. The implant of claim 3 or 4, wherein the implant is further sterilised.
6. The implant of claim 5, wherein the crystallinity is as measured after sterilisation.
7. The implant of claim 2 or 5, wherein said sterilisation is by means of irradiation.
8. The implant of any preceding claim, wherein said crosslinked ultrahigh molecular weight polyethylene is further characterized by (a) having been crosslinked with a peroxide concentration of 1 wt% and having a polymeric structure of 99.6% or almost 100% gel content, or (b) having been crosslinked with a peroxide concentration of 1 wt% followed by irradiation and having a polymeric structure of 97.5% gel content.
9. The implant of any preceding claim, wherein the crosslink is achieved according to the method selected from the group consisting of: chemically crosslinking a polyethylene, irradiation crosslinking a polyethylene in a molten state, and photocrosslinking a polyethylene in a molten state.
10. The implant of claim 7, wherein said implant is irradiated in the solid state.
11. The implant of claim 10, wherein said implant is irradiated in air with gamma-radiation at a dose of 34kGy.
12. The implant of any preceding claim, wherein said crosslinked ultrahigh molecular weight polyethylene is further characterized by having been annealed so as to shrink it to a stable size.
13. The implant of any preceding claim, wherein said crosslinked ultrahigh molecular weight polyethylene is further characterized by a polymeric structure of 3.35 degree of swelling provided by crosslinking with a peroxide concentration of 1wt% followed by irradiation, or a polymeric structure of 2.53 degree of swelling by crosslinking with a peroxide concentration of 1 wt%.
14. The implant of any preceding claim, wherein the implant is a component for use in a joint prosthesis.
15. The implant of claim 14, wherein the component is a bearing component.
16. The implant of claim 14 or 15, wherein the joint prosthesis is selected from the group consisting of: hip, knee, ankle, elbow, jaw, shoulder, finger joint prostheses and spine facet joint prostheses.
17. The implant of claim 16, wherein the joint prosthesis is selected from the group consisting of hip and knee joint prostheses.
18. The implant of claim 17, wherein the implant is selected from the group consisting of: an acetabular cup, an insert of an acetabular cup, and a liner of an acetabular cup.
19. An implantable bearing component with improved wear resistance, said implantable component comprising an irradiated crosslinked ultrahigh molecular weight polyethylene having increased wear resistance, and a polymeric

structure characterized by 28% to 51% crystallinity as measured by DSC.

20. The implantable bearing component of claim 19, wherein the component is further sterilised, the crystallinity being as measured after the sterilisation
- 5 21. An implantable bearing component with improved wear resistance, said implantable component comprising a crosslinked ultrahigh molecular weight polyethylene having increased wear resistance, said crosslinked ultrahigh, molecular weight polyethylene having a polymeric structure characterized by less than 45% crystallinity as measured by DSC.
- 10 22. The implantable bearing component of claim 21, wherein the crosslinked ultrahigh molecular weight polyethylene has a polymeric structure characterized by between 24% to 44% crystallinity as measured by DSC.
- 15 23. The implantable bearing component of claim 21 or 22, wherein the component is further sterilised.
24. The implantable bearing component of claim 23, wherein said crystallinity is as measured after sterilisation.
25. The implantable bearing component of claim 20 or 24, wherein said sterilisation is by means of irradiation.
- 20 26. The implantable bearing component of any one of claims 19 to 25, wherein the crosslinked ultrahigh molecular weight polyethylene has a polymeric structure characterized by a 3.35 degree of swelling provided by crosslinking with a peroxide concentration of 1 wt% followed by irradiation, or a polymeric structure of 2.53 degree of swelling by crosslinking with a peroxide concentration of 1wt%.
- 25 27. The implantable bearing component of any one of claims 19 to 26, wherein the crosslinked ultrahigh molecular weight polyethylene is further characterized by (a) having been crosslinked with a peroxide concentration of 1 wt% and having a polymeric structure of 99.6% or almost 100% gel content, or (b) having been crosslinked with a peroxide concentration of 1 wt% followed by irradiation and having a polymeric structure of 97.5% gel content.
- 30 28. The implantable bearing component of any one of claims 19 to 27, wherein the crosslink is achieved according to the method selected from the group consisting of: chemically crosslinking a polyethylene, irradiation crosslinking a polyethylene in a molten state, and photocrosslinking a polyethylene in a molten state.
- 35 29. The implantable bearing component of any one of claims 19 to 28, wherein the implantable bearing component is used in a joint prosthesis.
- 30 30. The implantable bearing component of claim 29, wherein the joint prosthesis is selected from the group consisting of: hip and knee joint prostheses.
- 40 31. The implantable bearing component of claim 30, wherein the implantable bearing component is selected from the group consisting of: an acetabular cup, an insert of an acetabular cup, and a liner of an acetabular cup.
- 45 32. A method of producing an implant with improved wear resistance, comprising the steps of: crosslinking a polyethylene to produce an irradiated crosslinked ultrahigh molecular weight polyethylene having a polymeric structure characterized by 28% to 51 % crystallinity as measured by DSC, and annealing the crosslinked ultrahigh molecular weight polyethylene to preshrink and stabilize its size before making it into an implant.
- 50 33. A method of producing an implant with improved wear resistance, comprising the steps of: crosslinking a polyethylene to produce a crosslinked ultrahigh molecular weight polyethylene having a polymeric structure characterized by less than 45% crystallinity as measured by DSC, and annealing the crosslinked ultrahigh molecular weight polyethylene to preshrink and stabilize its size before making it into an implant.
34. The method of claim 33, wherein the polymeric structure is characterized by between 24% to 44% crystallinity as measured by DSC.
- 55 35. The method of any one of claims 32 to 34 including a sterilisation step, wherein the crystallinity is as measured after the sterilisation step.

36. The method as claimed in claim 35, wherein the sterilisation step is achieved by means of irradiation.
37. The method of any one of claims 32 to 36, wherein the polymeric structure is characterized by a 3.35 degree of swelling provided by crosslinking with a peroxide concentration of 1 wt% and irradiation, or a 2.53 degree of swelling by crosslinking with a peroxide concentration of 1 wt%.
38. The method of any one of claims 32 to 37, wherein said crosslinked ultrahigh molecular weight polyethylene is further characterized by (a) having been crosslinked with a peroxide concentration of 1 wt% and having a polymeric structure of 99.6% or almost 100% gel content, or (b) having been crosslinked with a peroxide concentration of 1 wt% followed by irradiation and having a polymeric structure of 97.5% gel content.
39. The method of any one of claims 32 to 38, wherein the implant is a component for use in a joint prosthesis.
40. The method of any one of claims 32 to 39, wherein the implant is a bearing component.
41. The method of any one of claims 32 to 40, wherein the implant is selected from the group consisting of: an acetabular cup, an insert of an acetabular cup, and a liner of an acetabular cup.
42. A method for improving the wear resistance of an implant for use within a body, said implant being made from irradiated crosslinked ultrahigh molecular weight polyethylene, said method comprising the step of crosslinking a polyethylene to provide a polymeric structure of between 28% to 51% crystallinity as measured by DSC.
43. A method for improving the wear resistance of an implant for use within a body, said implant being made from ultrahigh molecular weight polyethylene, said method comprising the step of crosslinking a polyethylene to provide a polymeric structure with less than 45% crystallinity as measured by DSC.
44. The method of claim 43, wherein the polymeric structure is characterized by between 24% to 44% crystallinity as measured by DSC.
45. The method of any one of claims 42 to 44, further comprising the step of sterilising the implant, wherein the crystallinity is as measured after the sterilisation.
46. The method of claim 45, wherein the sterilisation is by means of irradiation.
47. The method of any one of claims 42 to 46, wherein the polymeric structure is characterized by a 3.35 degree of swelling provided by crosslinking with a peroxide concentration of 1 wt% and irradiation, or a 2.53 degree of swelling by crosslinking with a peroxide concentration of 1 wt%.
48. The method of any one of claims 42 to 47, wherein said crosslinked ultrahigh molecular weight polyethylene is further characterized by (a) having been crosslinked with a peroxide concentration of 1 wt% and having a polymeric structure of 99.6% or almost 100% gel content, or (b) having been crosslinked with a peroxide concentration of 1 wt% followed by irradiation and having a polymeric structure of 97.5% gel content.
49. The method of any one of claims 42 to 48, wherein the implant is a component for use in a joint prosthesis.
50. The method of any one of the claims 42 to 49, wherein the implant is a prosthetic bearing component.
51. The method of any one of the claims 42 to 50, wherein the implant is selected from the group consisting of: an acetabular cup, an insert of an acetabular cup, and a liner of an acetabular cup.
52. A method for making and improving wear resistance of an implant for use within a body, comprising the steps of: (a) crosslinking a polyethylene to provide an irradiated crosslinked ultrahigh molecular weight polyethylene with a polymeric structure of between 28% to 51% crystallinity as measured by DSC, and (b) forming the implant from said crosslinked ultrahigh molecular weight polyethylene.
53. A method for making and improving wear resistance of an implant for use within a body, comprising the steps of: (a) crosslinking a polyethylene to provide a crosslinked ultrahigh molecular weight polyethylene with a polymeric structure of less than 45% crystallinity as measured by DSC, and (b) forming the implant from said crosslinked

ultrahigh molecular weight polyethylene.

- 5 54. The method of claim 53, wherein the polymeric structure is characterized by between 24% to 44% crystallinity as measured by DSC.
- 10 55. The method of any one of claims 52 to 54, wherein the step of crosslinking further provides the crosslinked ultrahigh molecular weight polyethylene with a polymeric structure of 3.35 degree of swelling provided by crosslinking with a peroxide concentration of 1 wt% and irradiation, or a 2.53 degree of swelling provided by crosslinking with a peroxide concentration of 1wt%.
- 15 56. The method of any one of claims 52 to 55, wherein the step of crosslinking is (a) by crosslinking with a peroxide concentration of 1 wt% and further provides the ultrahigh molecular weight polyethylene with a polymeric structure of 99.6% or almost 100% gel content, or (b) by crosslinking with a peroxide coaccentration of 1 wt% followed by irradiation and further provides the ultrahigh molecular weight polyethylene with a polymeric structure of 97.5% gel content.
- 20 57. The method of any one of claims 52 to 56, wherein the implant is a component for use in a joint prosthesis.
- 25 58. The method of any one of the claims 52 to 57, wherein the implant is a prosthetic bearing component.
59. The method of any one of the claims 52 to 58, wherein the implant is selected from the group consisting of: an acetabular cup, an insert of an acetabular cup, and a liner of an acetabular cup.
60. The method of any one of the claims 52 to 59, further comprising the step of annealing the crosslinked ultrahigh molecular weight polyethylene at a temperature of 60°C to 120°C for 1 to 6 hours to stabilize its size.

Patentansprüche

- 30 1. Implantat zur Verwendung innerhalb eines Körpers, wobei das Implantat aus bestrahltem vernetzten ultrahochmolekularen Polyethylen mit einer polymeren Struktur von zwischen 28% und 51% Kristallinität, wie gemessen durch DSC, hergestellt ist, um die Verschleißbeständigkeit des Implantats innerhalb des Körpers zu verstärken.
- 35 2. Implantat nach Anspruch 1, wobei das Implantat weiterhin sterilisiert wird, wobei die Kristallinität wie nach der Sterilisation gemessen ist.
3. Implantat zur Verwendung innerhalb eines Körpers, wobei das Implantat aus einem vernetzten ultrahochmolekularen Polyethylen mit einer polymeren Struktur von weniger als 45% Kristallinität, wie gemessen durch DSC, hergestellt ist, um die Verschleißbeständigkeit des Implantats innerhalb des Körpers zu verstärken.
- 40 4. Implantat nach Anspruch 3, wobei das ultrahochmolekulare Polyethylen zwischen 24% und 44% Kristallinität, wie gemessen durch DSC, hat.
- 5 5. Implantat nach Anspruch 3 oder 4, wobei das Implantat weiterhin sterilisiert wird.
- 45 6. Implantat nach Anspruch 5, wobei die Kristallinität wie nach der Sterilisation gemessen ist.
7. Implantat nach Anspruch 2 oder 5, wobei die Sterilisation mittels Bestrahlung erfolgt.
- 50 8. Implantat nach einem vorhergehenden Anspruch, wobei das vernetzte ultrahochmolekulare Polyethylen weiter dadurch gekennzeichnet ist, daß es (a) mit einer Peroxidkonzentration von 1 Gew.-% vernetzt worden ist und eine polymere Struktur von 99,6% oder fast 100% Gelgehalt aufweist oder (b) mit einer Peroxidkonzentration von 1 Gew.-% und nachfolgender Bestrahlung vernetzt worden ist und eine polymere Struktur von 97,5% Gelgehalt aufweist.
- 55 9. Implantat nach einem vorhergehenden Anspruch, wobei die Vernetzung nach dem Verfahren, ausgewählt aus der Gruppe, bestehend aus: chemischer Vernetzung eines Polyethylens, Strahlenvernetzung eines Polyethylens in einem geschmolzenen Zustand und Photovernetzung eines Polyethylens in einem geschmolzenen Zustand, er-

reicht wird.

10. Implantat nach Anspruch 7, wobei das Implantat im festen Zustand bestrahlt wird.
11. Implantat nach Anspruch 10, wobei das Implantat in Luft mit Gamma-Bestrahlung mit einer Dosis von 34 kGy bestrahlt wird.
12. Implantat nach einem vorhergehenden Anspruch, wobei das vernetzte ultrahochmolekulare Polyethylen weiter dadurch gekennzeichnet ist, daß es getempert worden ist, um zu einer stabilen Größe zu schrumpfen.
13. Implantat nach einem vorhergehenden Anspruch, wobei das vernetzte ultrahochmolekulare Polyethylen weiter durch eine polymere Struktur mit einem Quellungsgrad von 3,35, bereitgestellt durch Vernetzen mit einer Peroxidkonzentration von 1 Gew.-% und nachfolgender Bestrahlung, oder eine polymere Struktur mit einem Quellungsgrad von 2,53 durch Vernetzen mit einer Peroxidkonzentration von 1 Gew.-% gekennzeichnet ist.
14. Implantat nach einem vorhergehenden Anspruch, wobei das Implantat eine Komponente zur Verwendung in einer Gelenkprothese ist.
15. Implantat nach Anspruch 14, wobei die Komponente eine Lagerkomponente ist.
16. Implantat nach Anspruch 14 oder 15, wobei die Gelenkprothese aus der Gruppe, bestehend aus: Hüft-, Knie-, Knöchel-, Ellenbogen-, Kiefer-, Schulter-, Fingergelenkprothesen und Wirbelsäulengelenkflächenprothesen, ausgewählt ist.
17. Implantat nach Anspruch 16, wobei die Gelenkprothese aus der Gruppe, bestehend aus: Hüft- und Kniegelenkprothesen, ausgewählt ist.
18. Implantat nach Anspruch 17, wobei das Implantat aus der Gruppe, bestehend aus: einer Hüftgelenkspfanne, einem Einsatz einer Hüftgelenkspfanne und einer Einlage einer Hüftgelenkspfanne, ausgewählt ist.
19. Implantierbare Lagerkomponente mit verbesserter Verschleißbeständigkeit, wobei die implantierbare Komponente ein bestrahltes vernetztes ultrahochmolekulares Polyethylen mit vermehrter Verschleißbeständigkeit und einer polymeren Struktur, gekennzeichnet durch 28% bis 51% Kristallinität, wie gemessen durch DSC, umfaßt.
20. Implantierbare Lagerkomponente nach Anspruch 19, wobei die Komponente weiterhin sterilisiert wird, wobei die Kristallinität wie nach der Sterilisation gemessen ist.
21. Implantierbare Lagerkomponente mit verbesserter Verschleißbeständigkeit, wobei die implantierbare Komponente ein vernetztes ultrahochmolekulares Polyethylen mit vermehrter Verschleißbeständigkeit umfaßt, wobei das vernetzte ultrahochmolekulare Polyethylen eine polymere Struktur, gekennzeichnet durch weniger als 45% Kristallinität, wie gemessen durch DSC, hat.
22. Implantierbare Lagerkomponente nach Anspruch 21, wobei das vernetzte ultrahochmolekulare Polyethylen eine polymere Struktur, gekennzeichnet durch zwischen 24% und 44% Kristallinität, wie gemessen durch DSC, hat.
23. Implantierbare Lagerkomponente nach Anspruch 21 oder 22, wobei die Komponente weiterhin sterilisiert wird.
24. Implantierbare Lagerkomponente nach Anspruch 23, wobei die Kristallinität wie nach der Sterilisation gemessen ist.
25. Implantierbare Lagerkomponente nach Anspruch 20 oder 24, wobei die Sterilisation mittels Bestrahlung erfolgt.
26. Implantierbare Lagerkomponente nach einem der Ansprüche 19 bis 25, wobei das vernetzte ultrahochmolekulare Polyethylen eine polymere Struktur, gekennzeichnet durch einen Quellungsgrad von 3,35, bereitgestellt durch Vernetzen mit einer Peroxidkonzentration von 1 Gew.-% und nachfolgender Bestrahlung, oder eine polymere Struktur mit einem Quellungsgrad von 2,53 durch Vernetzen mit einer Peroxidkonzentration von 1 Gew.-%, hat.
27. Implantierbare Lagerkomponente nach einem der Ansprüche 19 bis 26, wobei das vernetzte ultrahochmolekulare

Polyethylen weiter **dadurch gekennzeichnet ist, daß es** (a) mit einer Peroxidkonzentration von 1 Gew.-% vernetzt worden ist und eine polymere Struktur von 99,6% oder fast 100% Gelgehalt aufweist oder (b) mit einer Peroxidkonzentration von 1 Gew.-% und nachfolgender Bestrahlung vernetzt worden ist und eine polymere Struktur von 97,5% Gelgehalt aufweist.

5

28. Implantierbare Lagerkomponente nach einem der Ansprüche 19 bis 27, wobei die Vernetzung nach dem Verfahren, ausgewählt aus der Gruppe, bestehend aus: chemischer Vernetzung eines Polyethylens, Strahlenvernetzung eines Polyethylens in einem geschmolzenen Zustand und Photovernetzung eines Polyethylens in einem geschmolzenen Zustand, erreicht wird.
- 10 29. Implantierbare Lagerkomponente nach einem der Ansprüche 19 bis 28, wobei die implantierbare Lagerkomponente in einer Gelenkprothese verwendet wird.
- 15 30. Implantierbare Lagerkomponente nach Anspruch 29, wobei die Gelenkprothese aus der Gruppe, bestehend aus: Hüft- und Kniegelenkprothesen, ausgewählt ist.
- 20 31. Implantierbare Lagerkomponente nach Anspruch 30, wobei die implantierbare Lagerkomponente aus der Gruppe, bestehend aus: einer Hüftgelenkspfanne, einem Einsatz einer Hüftgelenkspfanne und einer Einlage einer Hüftgelenkspfanne, ausgewählt ist.
- 25 32. Verfahren zur Herstellung eines Implantats mit verbesserter Verschleißbeständigkeit, umfassend die Schritte: Vernetzen eines Polyethylens, um ein bestrahltes vernetztes ultrahochmolekulares Polyethylen mit einer polymeren Struktur, **gekennzeichnet durch** 28% bis 5 1% Kristallinität, wie gemessen **durch** DSC, zu erzeugen und Temperiern des vernetzten ultrahochmolekularen Polyethylens, um seine Größe vorzuschrumpfen und zu stabilisieren, bevor es zu einem Implantat verarbeitet wird.
- 30 33. Verfahren zur Herstellung eines Implantats mit verbesserter Verschleißbeständigkeit, umfassend die Schritte: Vernetzen eines Polyethylens, um ein vernetztes ultrahochmolekulares Polyethylen mit einer polymeren Struktur, **gekennzeichnet durch** weniger als 45% Kristallinität, wie gemessen **durch** DSC, zu erzeugen, und Temperiern des vernetzten ultrahochmolekularen Polyethylens, um seine Größe vorzuschrumpfen und zu stabilisieren, bevor es zu einem Implantat verarbeitet wird.
- 35 34. Verfahren nach Anspruch 33, wobei die polymere Struktur durch zwischen 24% und 44% Kristallinität, wie gemessen **durch** DSC, **gekennzeichnet** ist.
- 35 35. Verfahren nach einem der Ansprüche 32 bis 34 einschließlich eines Sterilisationsschrittes, wobei die Kristallinität wie nach dem Sterilisationsschritt gemessen ist.
- 40 36. Verfahren nach Anspruch 35, wobei der Sterilisationsschritt mittels Bestrahlung erreicht wird.
- 40 37. Verfahren nach einem der Ansprüche 32 bis 36, wobei die polymere Struktur durch einen Quellungsgrad von 3,35, bereitgestellt durch Vernetzen mit einer Peroxidkonzentration von 1 Gew.-% und Bestrahlung, oder einen Quellungsgrad von 2,53 durch Vernetzen mit einer Peroxidkonzentration von 1 Gew.-% **gekennzeichnet** ist.
- 45 38. Verfahren nach einem der Ansprüche 32 bis 37, wobei das vernetzte ultrahochmolekulare Polyethylen weiter **dadurch gekennzeichnet ist, daß es** (a) mit einer Peroxidkonzentration von 1 Gew.-% vernetzt worden ist und eine polymere Struktur von 99,6% oder fast 100% Gelgehalt aufweist oder (b) mit einer Peroxidkonzentration von 1 Gew.-% und nachfolgender Bestrahlung vernetzt worden ist und eine polymere Struktur von 97,5% Gelgehalt aufweist.
- 50 39. Verfahren nach einem der Ansprüche 32 bis 38, wobei das Implantat eine Komponente zur Verwendung in einer Gelenkprothese ist.
- 55 40. Verfahren nach einem der Ansprüche 32 bis 39, wobei das Implantat eine Lagerkomponente ist.
41. Verfahren nach einem der Ansprüche 32 bis 40, wobei das Implantat aus der Gruppe, bestehend aus: einer Hüftgelenkspfanne, einem Einsatz einer Hüftgelenkspfanne und einer Einlage einer Hüftgelenkspfanne, ausgewählt ist.

42. Verfahren zur Verbesserung der Verschleißbeständigkeit eines Implantats zur Verwendung innerhalb eines Körpers, wobei das Implantat aus bestrahltem vernetzten ultrahochmolekularen Polyethylen hergestellt ist, wobei das Verfahren den Schritt der Vernetzung eines Polyethylens umfaßt, um eine polymere Struktur zwischen 28% und 51% Kristallinität wie gemessen durch DSC, bereitzustellen.
- 5 43. Verfahren zur Verbesserung der Verschleißbeständigkeit eines Implantats zur Verwendung innerhalb eines Körpers, wobei das Implantat aus bestrahltem vernetzten ultrahochmolekularen Polyethylen hergestellt ist, wobei das Verfahren den Schritt der Vernetzung eines Polyethylens umfaßt, um eine polymere Struktur mit weniger als 45% Kristallinität, wie gemessen durch DSC, bereitzustellen.
- 10 44. Verfahren nach Anspruch 43, wobei die polymere Struktur durch zwischen 24% und 44% Kristallinität, wie gemessen durch DSC, gekennzeichnet ist.
- 15 45. Verfahren nach einem der Ansprüche 42 bis 44, weiterhin umfassend den Schritt der Sterilisierung des Implantats, wobei die Kristallinität wie nach der Sterilisation gemessen ist.
46. Verfahren nach Anspruch 45, wobei die Sterilisation mittels Bestrahlung erfolgt.
- 20 47. Verfahren nach einem der Ansprüche 42 bis 46, wobei die polymere Struktur durch einen Quellungsgrad von 3,35, bereitgestellt durch Vernetzen mit einer Peroxidkonzentration von 1 Gew.-% und Bestrahlung, oder einen Quellungsgrad von 2,53 durch Vernetzen mit einer Peroxidkonzentration von 1 Gew.-% gekennzeichnet ist.
- 25 48. Verfahren nach einem der Ansprüche 42 bis 47, wobei das vernetzte ultrahochmolekulare Polyethylen weiter dadurch gekennzeichnet ist, daß es (a) mit einer Peroxidkonzentration von 1 Gew.-% vernetzt worden ist und eine polymere Struktur von 99,6% oder fast 100% Gelgehalt aufweist oder (b) mit einer Peroxidkonzentration von 1 Gew.-% und nachfolgender Bestrahlung vernetzt worden ist und eine polymere Struktur von 97,5% Gelgehalt aufweist.
- 30 49. Verfahren nach einem der Ansprüche 42 bis 48, wobei das Implantat eine Komponente zur Verwendung in einer Gelenkprothese ist.
- 50 50. Verfahren nach einem der Ansprüche 42 bis 49, wobei das Implantat eine prothetische Lagerkomponente ist.
- 35 51. Verfahren nach einem der Ansprüche 42 bis 50, wobei das Implantat aus der Gruppe, bestehend aus: einer Hüftgelenkspfanne, einem Einsatz einer Hüftgelenkspfanne und einer Einlage einer Hüftgelenkspfanne, ausgewählt ist.
- 40 52. Verfahren zur Herstellung und Verbesserung der Verschleißfestigkeit eines Implantats zur Verwendung innerhalb eines Körpers, umfassend die Schritte: (a) Vernetzen eines Polyethylens, um ein bestrahltes vernetztes ultrahochmolekulares Polyethylen mit einer polymeren Struktur von zwischen 28% und 51% Kristallinität, wie gemessen durch DSC, bereitzustellen, und (b) Erzeugen des Implantats aus dem vernetzten ultrahochmolekularen Polyethylen.
- 45 53. Verfahren zur Herstellung und Verbesserung der Verschleißfestigkeit eines Implantats zur Verwendung innerhalb eines Körpers, umfassend die Schritte: (a) Vernetzen eines Polyethylens, um ein vernetztes ultrahochmolekulares Polyethylen mit einer polymeren Struktur von weniger als 45% Kristallinität, wie gemessen durch DSC, bereitzustellen, und (b) Erzeugen des Implantats aus dem vernetzten ultrahochmolekularen Polyethylen.
- 50 54. Verfahren nach Anspruch 53, wobei die polymere Struktur durch zwischen 24% und 44% Kristallinität, wie gemessen durch DSC, gekennzeichnet ist.
- 55 55. Verfahren nach einem der Ansprüche 52 bis 54, wobei der Schritt der Vernetzung weiterhin das vernetzte ultrahochmolekulare Polyethylen mit einer polymeren Struktur mit einem Quellungsgrad von 3,35, bereitgestellt durch Vernetzen mit einer Peroxidkonzentration von 1 Gew.-% und Bestrahlung, oder einem Quellungsgrad von 2,53, bereitgestellt durch Vernetzen mit einer Peroxidkonzentration von 1 Gew.-%, bereitstellt.
56. Verfahren nach einem der Ansprüche 52 bis 55, wobei der Schritt der Vernetzung (a) durch Vernetzen mit einer Peroxidkonzentration von 1 Gew.-% erfolgt und weiterhin das ultrahochmolekulare Polyethylen mit einer polymeren

Struktur von 99,6% oder fast 100% Gelgehalt bereitstellt oder (b) durch Vernetzen mit einer Peroxidkonzentration von 1 Gew.-% und nachfolgender Bestrahlung erfolgt und weiterhin das ultrahochmolekulare Polyethylen mit einer polymeren Struktur von 97,5% Gelgehalt bereitstellt.

- 5 57. Verfahren nach einem der Ansprüche 52 bis 56, wobei das Implantat eine Komponente zur Verwendung in einer Gelenkprothese ist.
- 58. Verfahren nach einem der Ansprüche 52 bis 57, wobei das Implantat eine prothetische Lagerkomponente ist.
- 10 59. Verfahren nach einem der Ansprüche 52 bis 58, wobei das Implantat aus der Gruppe, bestehend aus: einer Hüftgelenkspfanne, einem Einsatz einer Hüftgelenkspfanne und einer Einlage einer Hüftgelenkspfanne, ausgewählt ist.
- 15 60. Verfahren nach einem der Ansprüche 52 bis 59, weiterhin umfassend den Schritt des Temperns des vernetzten ultrahochmolekularen Polyethylens bei einer Temperatur von 60°C bis 120°C für 1 bis 6 Stunden, um seine Größe zu stabilisieren.

Revendications

- 20 1. Implant à utiliser dans un corps, ledit implant étant fait de polyéthylène de poids moléculaire ultra élevé, réticulé, irradié, ayant une structure polymère d'une cristallinité d'entre 28% et 51%, telle que mesurée par DSC, de manière à augmenter la résistance à l'usure dudit implant dans le corps.
- 25 2. L'implant de la revendication 1, où l'implant est en outre stérilisé, la cristallinité étant mesurée après la stérilisation.
- 30 3. Implant à utiliser dans un corps, ledit implant étant fait d'un polyéthylène de poids moléculaire ultra élevé, réticulé, irradié, ayant une structure polymère d'une cristallinité de moins de 45%, telle que mesurée par DSC, de manière à augmenter la résistance à l'usure dudit implant dans le corps.
- 35 4. L'implant de la revendication 3, où ledit polyéthylène de poids moléculaire ultra élevé a une cristallinité d'entre 24% et 44%, telle que mesurée par DSC.
- 5. L'implant de la revendication 3 ou 4, où l'implant est en outre stérilisé.
- 35 6. L'implant de la revendication 5, où la cristallinité est telle que mesurée après la stérilisation.
- 7. L'implant de la revendication 2 ou 5, où ladite stérilisation est faite par irradiation.
- 40 8. L'implant de l'une quelconque des revendications précédentes, où ledit polyéthylène de poids moléculaire ultra élevé, réticulé, est caractérisé en outre, (a) en ayant été réticulé avec une concentration de peroxyde de 1% en poids et en ayant une structure polymère d'une teneur en gel de 99,6% ou de presque 100%, ou (b) en ayant été réticulé avec une concentration de peroxyde de 1% en poids, suivi par l'irradiation et en ayant une structure polymère d'une teneur en gel de 97,5%.
- 45 9. L'implant de l'une quelconque des revendications précédentes, où la réticulation est réalisée selon le procédé sélectionné parmi le groupe consistant à: réticuler chimiquement un polyéthylène, réticuler par irradiation un polyéthylène dans un état fondu, et photoréticuler un polyéthylène dans un état fondu.
- 50 10. L'implant de la revendication 7, où ledit implant est irradié à l'état solide.
- 11. L'implant de la revendication 10, où ledit implant est irradié à l'air avec un rayonnement gamma à une dose de 34 kGy.
- 55 12. L'implant de l'une quelconque des revendications précédentes, où ledit polyéthylène de poids moléculaire ultra élevé, réticulé, est en outre caractérisé en ayant été recuit de manière à le rétrécir à une dimension stable.
- 13. L'implant de l'une quelconque des revendications précédentes, où ledit polyéthylène de poids moléculaire ultra

élevé, réticulé, est en outre **caractérisé par** une structure polymère d'un degré de gonflement de 3,35 fourni par la réticulation avec une concentration de peroxyde de 1% en poids, suivie par l'irradiation, ou par une structure polymère d'un degré de gonflement de 2,53 par la réticulation avec une concentration de peroxyde de 1% en poids.

- 5 14. L'implant de l'une quelconque des revendications précédentes, où l'implant est un composant à utiliser dans une prothèse articulaire.
- 10 15. L'implant de la revendication 14, où le composant est un composant porteur.
- 15 16. L'implant de la revendication 14 ou 15, où la prothèse articulaire est sélectionnée du groupe consistant en: prothèses articulaires de la hanche, du genou, de la cheville, du coude, de la mâchoire, de l'épaule, du doigt et en prothèses articulaires facettaires rachidiennes.
- 15 17. L'implant de la revendication 16, où la prothèse articulaire est sélectionnée parmi le groupe consistant en: prothèses articulaires de la hanche et du genou.
- 20 18. L'implant de la revendication 17, où l'implant est sélectionné parmi le groupe consistant en: une cupule cotyloïdienne, un insert de cupule cotyloïdienne et une garniture de cupule cotyloïdienne.
- 25 19. Composant porteur implantable avec une résistance à l'usure améliorée, ledit composant implantable comprenant un polyéthylène de poids moléculaire ultra élevé, réticulé, irradié, ayant une résistance à l'usure augmentée, et une structure polymère **caractérisée par** une cristallinité de 28% à 51%, telle que mesurée par DSC.
- 25 20. Le composant porteur implantable de la revendication 19, où le composant est en outre stérilisé, la cristallinité étant telle que mesurée après la stérilisation.
- 30 21. Composant porteur implantable avec une résistance à l'usure améliorée, ledit composant implantable comprenant un polyéthylène de poids moléculaire ultra élevé, réticulé, ayant une résistance à l'usure augmentée, ledit polyéthylène de poids moléculaire ultra élevé, réticulé, ayant une structure polymère **caractérisée par** une cristallinité de moins de 45%, telle que mesurée par DSC.
- 35 22. Le composant porteur implantable de la revendication 21, où le polyéthylène de poids moléculaire ultra élevé, réticulé, a une structure polymère **caractérisée par** une cristallinité d'entre 24% et 44%, telle que mesurée par DSC.
- 35 23. Le composant porteur implantable de la revendication 21 ou 22, où le composant est en outre stérilisé.
- 40 24. Le composant porteur implantable de la revendication 23, où ladite cristallinité est telle que mesurée après la stérilisation.
- 40 25. Le composant porteur implantable de la revendication 20 ou 24, où ladite stérilisation est faite par irradiation.
- 45 26. Le composant porteur implantable de l'une quelconque des revendications 19 à 25, où le polyéthylène de poids moléculaire ultra élevé, réticulé, a une structure polymère **caractérisée par** un degré de gonflement de 3,35 fourni par la réticulation avec une concentration de peroxyde de 1% en poids, suivie par l'irradiation, ou une structure polymère d'un degré de gonflement de 2,53 par la réticulation avec une concentration de peroxyde de 1% en poids.
- 50 27. Le composant porteur implantable de l'une quelconque des revendications 19 à 26, où le polyéthylène de poids moléculaire ultra élevé, réticulé, est **caractérisé en** outre (a) en ayant été réticulé avec une concentration de peroxyde de 1% en poids et en ayant une structure polymère d'une teneur en gel de 99,6% ou de presque 100%, ou (b) en ayant été réticulé avec une concentration de peroxyde de 1% en poids, suivi par l'irradiation et en ayant une structure polymère d'une teneur en gel de 97,5%.
- 55 28. Le composant porteur implantable de l'une quelconque des revendications 19 à 27, où la réticulation est réalisée selon le procédé sélectionné parmi le groupe consistant à: réticuler chimiquement un polyéthylène, réticuler par irradiation un polyéthylène dans un état fondu, et photoréticuler un polyéthylène dans un état fondu.

29. Le composant porteur implantable de l'une quelconque des revendications 19 à 28, où le composant porteur implantable est utilisé dans une prothèse articulaire.
- 5 30. Le composant porteur implantable de la revendication 29, où la prothèse articulaire est sélectionnée parmi le groupe consistant en: prothèses articulaires de la hanche et du genou.
- 10 31. Le composant porteur implantable de la revendication 30, où le composant porteur implantable est sélectionné parmi le groupe consistant en: une cupule cotyloïdienne, un insert de cupule cotyloïdienne et une garniture de cupule cotyloïdienne.
- 15 32. Procédé de production d'un implant avec une résistance à l'usure améliorée, comprenant les étapes consistant à: réticuler un polyéthylène pour produire un polyéthylène de poids moléculaire ultra élevé, réticulé, irradié, ayant une structure polymère **caractérisée par** une cristallinité de 28% à 51%, telle que mesurée par DSC, et recuire le polyéthylène de poids moléculaire ultra élevé, réticulé, pour prérétrécir et stabiliser sa dimension avant de le transformer en un implant.
- 20 33. Procédé de production d'un implant avec une résistance à l'usure améliorée, comprenant les étapes consistant à: réticuler un polyéthylène pour produire un polyéthylène de poids moléculaire ultra élevé, réticulé, irradié, ayant une structure polymère **caractérisée par** une cristallinité de moins de 45%, telle que mesurée par DSC, et recuire le polyéthylène de poids moléculaire ultra élevé, réticulé, pour prérétrécir et stabiliser sa dimension avant de le transformer en un implant.
- 25 34. Le procédé de la revendication 33, où la structure polymère est **caractérisée par** une cristallinité d'entre 24% et 44%, telle que mesurée par DSC.
35. Le procédé de l'une quelconque des revendications 32 à 34 comprenant une étape de stérilisation, où la cristallinité est telle que mesurée après l'étape de stérilisation.
- 30 36. Le procédé tel que revendiqué dans la revendication 35, où l'étape de stérilisation est réalisée par irradiation.
- 35 37. Le procédé de l'une quelconque des revendications 32 à 36, où la structure polymère est **caractérisée par** un degré de gonflement de 3,35 fourni par la réticulation avec une concentration de peroxyde de 1% en poids et l'irradiation, ou un degré de gonflement de 2,53 par la réticulation avec une concentration de peroxyde de 1% en poids.
- 40 38. Le procédé de l'une quelconque des revendications 32 à 37, où ledit polyéthylène de poids moléculaire ultra élevé, réticulé, est **caractérisé en outre** (a) en ayant été réticulé avec une concentration de peroxyde de 1% en poids et en ayant une structure polymère d'une teneur en gel de 99,6% ou de presque 100%, ou (b) en ayant été réticulé avec une concentration de peroxyde de 1% en poids, suivi par l'irradiation et en ayant une structure polymère d'une teneur en gel de 97,5%.
39. Le procédé de l'une quelconque des revendications 32 à 38, où l'implant est un composant à utiliser dans une prothèse articulaire.
- 45 40. Le procédé de l'une quelconque des revendications 32 à 39, où l'implant est un composant porteur.
41. Le procédé de l'une quelconque des revendications 32 à 40, où l'implant est sélectionné parmi le groupe consistant en: une cupule cotyloïdienne, un insert de cupule cotyloïdienne et une garniture de cupule cotyloïdienne.
- 50 42. Procédé pour améliorer la résistance à l'usure d'un implant à utiliser dans un corps, ledit implant étant fait de polyéthylène de poids moléculaire ultra élevé, réticulé, irradié, ledit procédé comprenant l'étape consistant à réticuler un polyéthylène pour donner une structure polymère d'une cristallinité d'entre 28% et 51 %, telle que mesurée par DSC.
- 55 43. Procédé pour améliorer la résistance à l'usure d'un implant à utiliser dans un corps, ledit implant étant fait de polyéthylène de poids moléculaire ultra élevé, réticulé, irradié, ledit procédé comprenant l'étape consistant à réticuler un polyéthylène pour donner une structure polymère avec une cristallinité de moins de 45%, telle que mesurée par DSC.

44. Le procédé de la revendication 43, où la structure polymère est **caractérisée par** une cristallinité d'entre 24% et 44%, telle que mesurée par DSC.
- 5 45. Le procédé de l'une quelconque des revendications 42 à 44, comprenant en outre l'étape consistant à stériliser l'implant, où la cristallinité est telle que mesurée après la stérilisation.
46. Le procédé de la revendication 45, où la stérilisation est faite par irradiation
- 10 47. Le procédé de l'une quelconque des revendications 42 à 46, où la structure polymère est **caractérisée par** un degré de gonflement de 3,35 fourni par la réticulation avec une concentration de peroxyde de 1% en poids et l'irradiation, ou un degré de gonflement de 2,53 par la réticulation avec une concentration de peroxyde de 1% en poids.
- 15 48. Le procédé de l'une quelconque des revendications 42 à 47, où ledit polyéthylène de poids moléculaire ultra élevé, réticulé, est **caractérisé en outre** (a) en ayant été réticulé avec une concentration de peroxyde de 1% en poids et en ayant une structure polymère d'une teneur en gel de 99,6% ou de presque 100%, ou (b) en ayant été réticulé avec une concentration de peroxyde de 1% en poids, suivi par l'irradiation et en ayant une structure polymère d'une teneur en gel de 97,5%.
- 20 49. Le procédé de l'une quelconque des revendications 42 à 48, où l'implant est un composant à utiliser dans une prothèse articulaire.
50. Le procédé de l'une quelconque des revendications 42 à 49, où l'implant est un composant prothétique porteur.
- 25 51. Le procédé de l'une quelconque des revendications 42 à 50, où l'implant est sélectionné parmi le groupe consistant en: une cupule cotyloïdienne, un insert de cupule cotyloïdienne et une garniture de cupule cotyloïdienne.
- 30 52. Procédé pour faire et améliorer la résistance à l'usure d'un implant à utiliser dans un corps, comprenant les étapes consistant à: (a) réticuler un polyéthylène pour fournir un polyéthylène de poids moléculaire ultra élevé, réticulé, irradié, avec une structure polymère d'une cristallinité d'entre 28% et 51%, telle que mesurée par DSC, et (b) former l'implant avec ledit polyéthylène de poids moléculaire ultra élevé, réticulé.
- 35 53. Procédé pour faire et améliorer la résistance à l'usure d'un implant à utiliser dans un corps, comprenant les étapes consistant à: (a) réticuler un polyéthylène en un polyéthylène de poids moléculaire ultra élevé, réticulé, irradié avec une structure polymère d'une cristallinité de moins de 45%, telle que mesurée par DSC, et (b) former l'implant avec ledit polyéthylène de poids moléculaire ultra élevé, réticulé.
- 40 54. Le procédé de la revendication 53, où la structure polymère est **caractérisée par** une cristallinité d'entre 24% et 44%, telle que mesurée par DSC.
- 45 55. Le procédé de l'une quelconque des revendications 52 à 54, où l'étape de réticulation fournit en outre au polyéthylène de poids moléculaire ultra élevé, réticulé, une structure polymère d'un degré de gonflement de 3,35 fourni par la réticulation avec une concentration de peroxyde de 1% en poids et l'irradiation, ou un degré de gonflement de 2,53 fourni par la réticulation avec une concentration de peroxyde de 1% en poids.
- 50 56. Le procédé de l'une quelconque des revendications 52 à 55, où l'étape de réticulation se fait (a) par la réticulation avec une concentration de peroxyde de 1% en poids et fournit en outre au polyéthylène de poids moléculaire ultra élevé, une structure polymère d'une teneur en gel de 99,6% ou de presque 100%, ou (b) par la réticulation avec une concentration de peroxyde de 1% en poids suivie par l'irradiation, et fournit en outre au polyéthylène de poids moléculaire ultra élevé, une structure polymère d'une teneur en gel de 97,5%.
- 55 57. Le procédé de l'une quelconque des revendications 52 à 56, où l'implant est un composant à utiliser dans une prothèse articulaire.
58. Le procédé de l'une quelconque des revendications 52 à 57, où l'implant est un composant prothétique porteur.
59. Le procédé de l'une quelconque des revendications 52 à 58, où l'implant est sélectionné parmi le groupe consistant en: une cupule cotyloïdienne, un insert de cupule cotyloïdienne et une garniture de cupule cotyloïdienne.

EP 0 722 973 B1

60. Le procédé de l'une quelconque des revendications 52 à 59, comprenant en outre l'étape consistant à recuire le polyéthylène de poids moléculaire ultra élevé, réticulé, à une température de 60°C à 120°C pendant 1 à 6 heures pour en stabiliser la dimension.

5

10

15

20

25

30

35

40

45

50

55

FIG. 1A

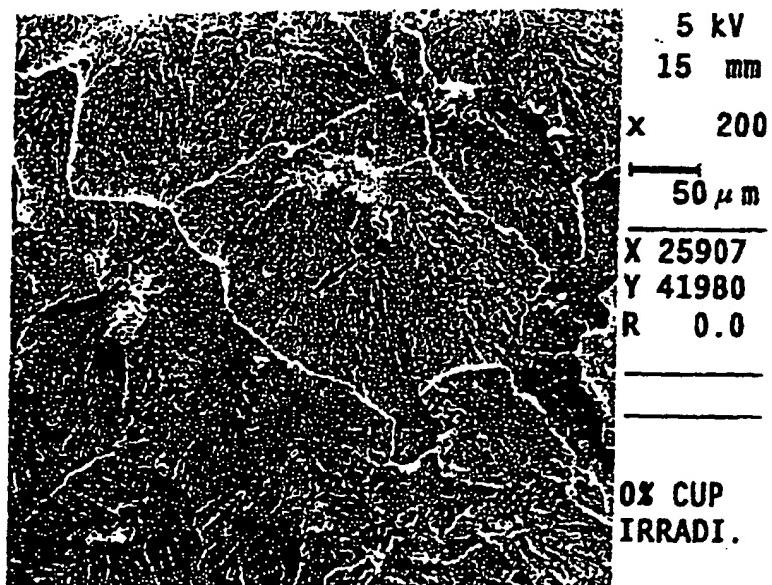


FIG. 1B

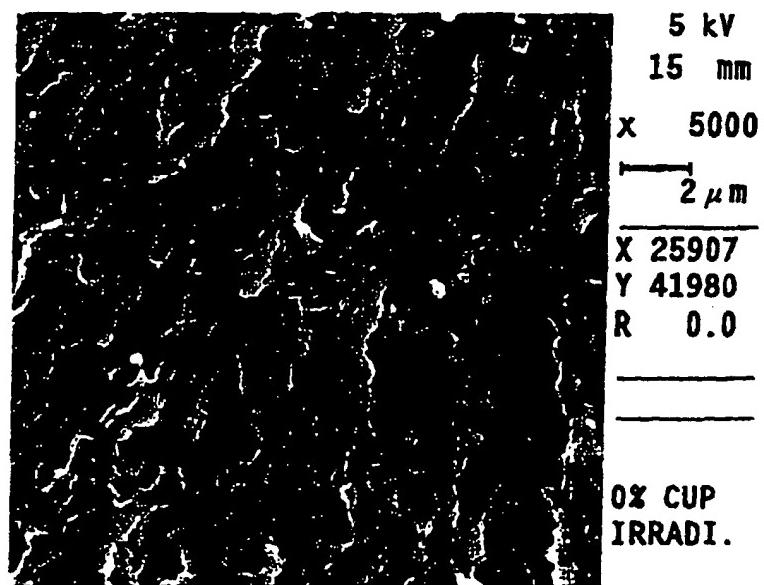


FIG. 2A

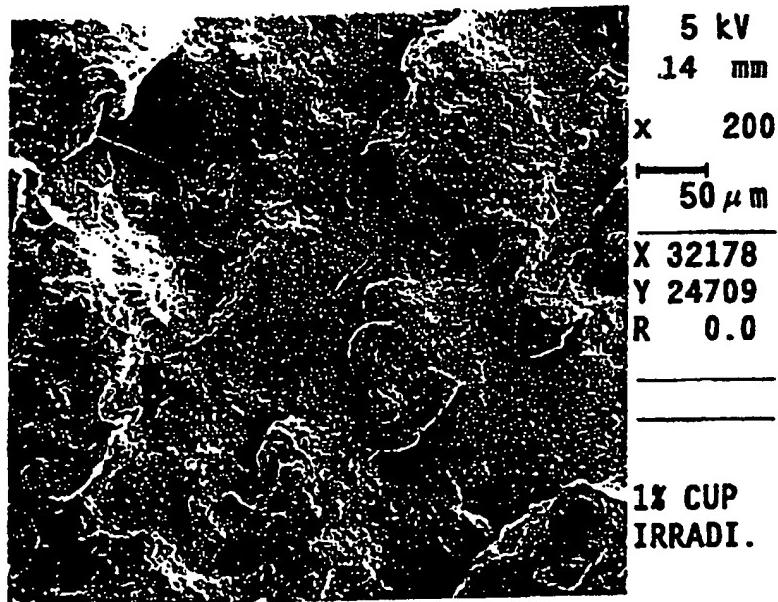


FIG. 2B

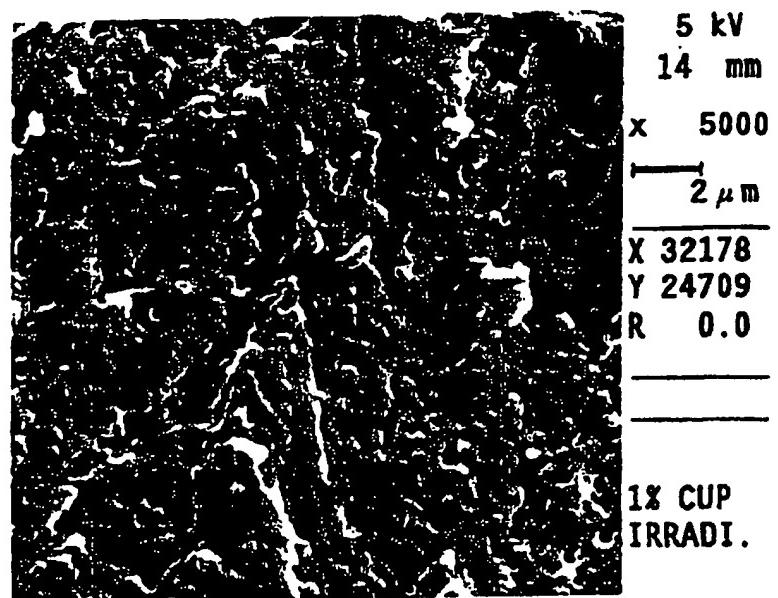


FIG. 3A

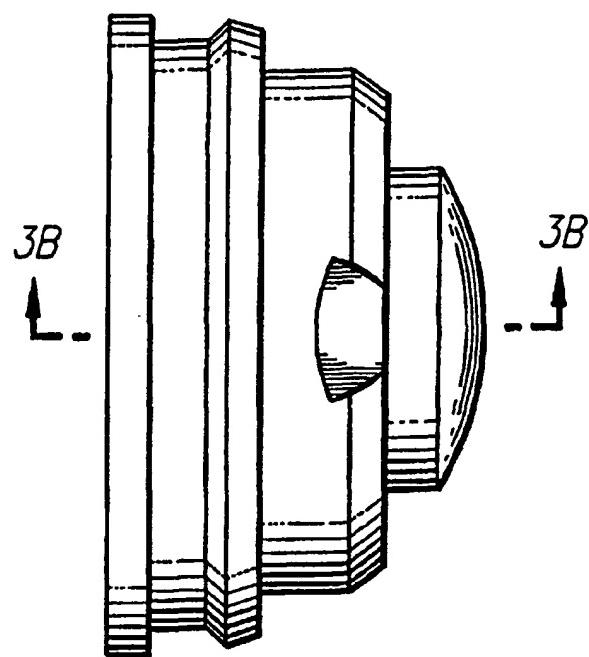


FIG. 3B

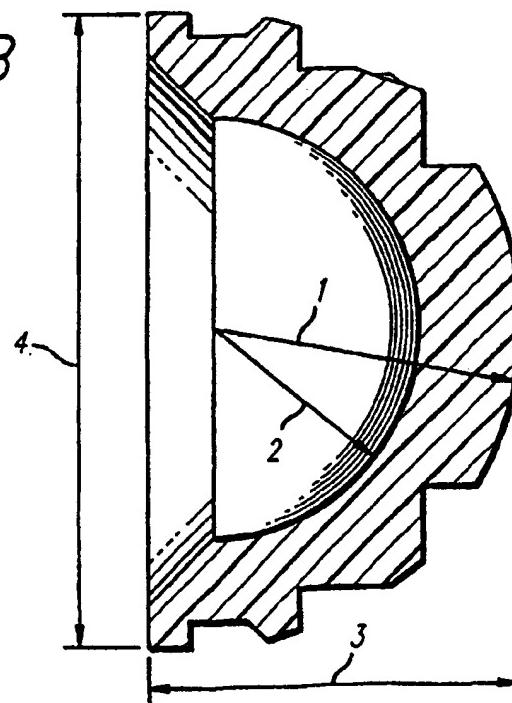


FIG. 4

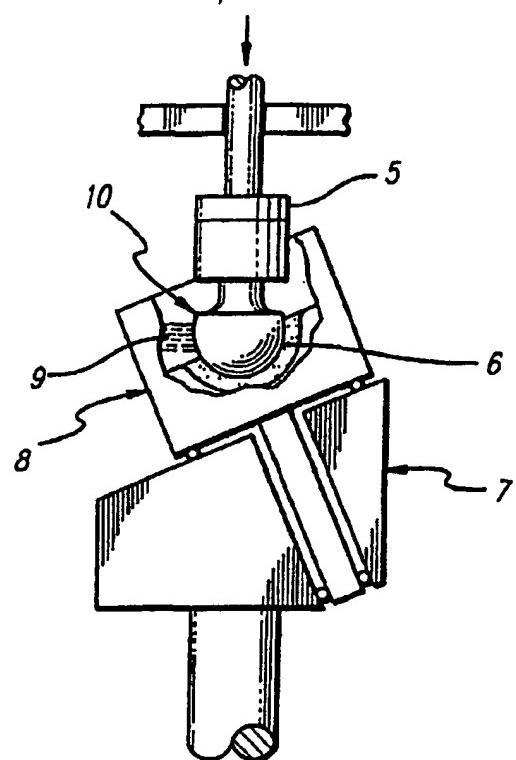


FIG. 5

